The Series of Rare Earth Zinc Phosphides RZn_3P_3 (R = Y, La–Nd, Sm, Gd–Er) and the Corresponding Cadmium Compound $PrCd_3P_3$

André T. Nientiedt and Wolfgang Jeitschko[1]

Anorganisch–Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany

DEDICATED TO PROFESSOR ARTHUR W. SLEIGHT ON THE OCCASION OF HIS 60TH BIRTHDAY

The 12 title compounds were prepared by reaction of the elemental components in a NaCl/KCl flux. Their isotypic crystal structures were determined for the two praseodymium compounds from single-crystal X-ray data in the space group $P6_3/mmc$ with $Z = 2$ formula units per cell; $PrZn_3P_3$: $a = 404.0(1)$ pm, $c = 1997.9(6)$ pm, $R = 0.064$ for 253 structure factors; $PrCd_3P_3$: $a = 426.5(1)$ pm, $c = 2090.6(6)$ pm, $R = 0.020$ for 309 F values and 14 variables each. Large displacement parameters for one-third of the zinc, cadmium, and phosphorus sites of both structures indicate distortions. Hence, the true symmetry of both compounds may be lower, as is known for the closely related structure of $ScAl_3C_3$. The cadmium and phosphorus atoms of $PrCd_3P_3$ form triple-layers similar to the layers in the wurtzite-type structure of ZnS. These nets are separated from each other by the praseodymium atoms. The praseodymium and cadmium atoms form close-packed layers of the stacking sequence $(hccc)_2$ corresponding to the atomic layers $(CdCdPrCd)_2$. The phosphorus atoms occupy octahedral and trigonal bipyramidal voids of the kind Pr_3Cd_3 and Cd_5, respectively. Chemical bonding is briefly discussed. The praseodymium and cadmium atoms obtain their usual oxidation numbers corresponding to the formula $Pr^{3+}(Cd^{2+})_3(P^{3-})_3$. © 1999 Academic Press

INTRODUCTION

We have recently reported on a new ternary arsenide with the composition $Pr_3Zn_2As_6$, which crystallizes with a vacancy variant of the $HfCuSi_2$ type structure (1). The latter structure has also been found for quaternary compounds, e.g., for the series $LnZnPnO$ (Ln = lanthanoids, Pn = P, As, Sb) (2, 3). In searching for compounds with related composition we found the ternary phosphides of the present paper. They seem to be the first ternary pnictides which are (almost) isotypic with a ternary carbide. After completion of the work reported here, we became aware of a publication on $SmZn_3P_3$. This compound is completely isotypic with the phosphides reported here, although the structure of $SmZn_3P_3$ has been described with the lower symmetry space group $P6_322$ (4).

SAMPLE PREPARATION AND LATTICE CONSTANTS

The ternary phosphides were prepared by reaction of the elemental components in the atomic ratio 1:3:3 in a salt flux. About 0.5 g of the mixed elements were sealed in evacuated silica tubes together with about 2 g of the flux (NaCl/KCl = 1:1). The rare earth elements were purchased in the form of ingots (nominal purity 99.9%). Filings of these were prepared under dry (Na) paraffin oil. The oil was removed by dry hexane and the filings were stored under vacuum. They were only briefly exposed to air prior to the reactions. Elemental zinc (Merck, 99.9%) and cadmium (Alfa, m2N5) were purchased as powders. Red phosphorus (Hoechst, Werk Knapsack) was obtained in the form of compact pieces in "ultrapure" (semiconductor grade) quality.

In order to allow a controlled reaction of the phosphorus the samples were first annealed for one day at 500°C, followed by 7–10 days at 800°C. They were then quenched on air. The silica tubes were not visibly attacked under these annealing conditions. The salt matrix was dissolved in distilled water and the products were cleaned and dried in aceton.

The ternary phosphides were obtained in the form of very small hexagonal platelets with metallic luster like silicon crystals. In powdered form they are black. They are stable in air for long periods of time. Energy dispersive X-ray fluorescence analyses (EDX) in a scanning electron microscope did not reveal any impurity elements (like silicon) heavier than sodium.

All products were characterized through their Guinier powder diagrams, which were recorded with $CuK\alpha_1$ radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. Indices to these patterns were assigned on the basis of the diagrams calculated (5) using the positional

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[1] To whom correspondence should be addresed.

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TABLE 1
Lattice Constants of the Hexagonal Compounds RZn_3P_3 and $PrCd_3P_3$[a]

Compound	a (pm)	c (pm)	c/a	V (nm^3)
YZn_3P_3	398.8(1)	1983.7(5)	4.974	0.2732
$LaZn_3P_3$	406.5(1)	2012.9(5)	4.952	0.2881
$CeZn_3P_3$	405.1(1)	2001.9(5)	4.942	0.2845
$PrZn_3P_3$	404.0(1)	1997.9(6)	4.945	0.2824
$NdZn_3P_3$	403.3(1)	1994.2(6)	4.945	0.2809
$SmZn_3P_3$	401.9(1)	1988.5(4)	4.948	0.2781
$SmZn_3P_3$[b]	401.67(4)	1987.54(1)	4.948	0.2777
$GdZn_3P_3$	400.4(1)	1985.5(5)	4.959	0.2757
$TbZn_3P_3$	399.6(1)	1982.5(4)	4.961	0.2742
$DyZn_3P_3$	398.8(1)	1978.4(6)	4.961	0.2725
$HoZn_3P_3$	397.9(1)	1978.5(5)	4.972	0.2713
$ErZn_3P_3$	397.6(2)	1975.6(8)	4.969	0.2705
$PrCd_3P_3$	426.5(1)	2090.6(6)	4.902	0.3293

[a] Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.
[b] Lattice constants from Ref. 4.

TABLE 2
Crystal Data for $PrZn_3P_3$ and $PrCd_3P_3$

Compound	$PrZn_3P_3$	$PrCd_3P_3$
Space group	$P6_3/mmc$	$P6_3/mmc$
	(No. 194)	(No. 194)
Cell constants (pm)	$a = 403.8(1)$	$a = 426.5(1)$
	$c = 1994.2(5)$	$c = 2089.7(2)$
Cell volume (nm^3)	0.2816	0.3292
Formula units per cell	$Z = 2$	$Z = 2$
Formula mass	430.0	571.1
Calculated density (g/cm^3)	$\rho_{calc} = 5.06$	$\rho_{calc} = 5.76$
Crystal size (µm^3)	$75 \times 50 \times 10$	$50 \times 35 \times 17$
Range in h, k, l	$\pm 7, \pm 7, 0–36$	$\pm 7, \pm 7, 0–37$
Scan range	$4° < 2\theta < 80°$	$4° < 2\theta < 80°$
Highest/lowest transmission	1.15	1.60
Total no. of reflections	3579	4176
Data after averaging	398	455
Inner residual (on F^2 values)	$R_i = 0.180$	$R_i = 0.086$
Unique reflections with $I > 2\sigma(I)$	253	309
Number of variables	14	14
Weighted residual (on F^2)	$R_w = 0.140$	$R_w = 0.045$
Conventional residual with $F > 2\sigma(F)$	$R = 0.064$	$R = 0.020$

parameters as obtained from the structure determinations of $PrZn_3P_3$ and $PrCd_3P_3$. The lattice constants (Table 1) were refined by least-squares fits.

STRUCTURE DETERMINATION

Single crystals of $PrZn_3P_3$ and $PrCd_3P_3$ were selected under a microscope and their quality was checked by Laue patterns. Intensity data were recorded on a four-circle X-ray diffractometer (Enraf–Nonius, CAD4) using graphite-monochromated Mo$K\alpha$ radiation and a scintillation counter with pulse-height discrimination. Background counts were recorded at both ends of each $\theta/2\theta$ scan. Absorption corrections were applied on the basis of psi scan data. The lattice constants obtained from the four-circle diffractometer data (Table 2) were in good agreement with those calculated from the powder data. In general, they are slightly smaller than those of the powder data, because of systematic errors of the single-crystal data due to absorption. Further details of the data collections and some results are summerized in Table 2.

The diffractometer data revealed the Laue symmetry $6/mmm$ with lattice constants similar to those of the carbides $ScAl_3C_3$ (6, 7) and UAl_3C_3 (7, 8), recently investigated in our laboratory. This suggested the crystal structures of the new phosphides to be similar to those of the previously reported carbides. Hence, the positional parameters of the carbide structure were used as starting parameters for the least-squares refinements with the program SHELXL-93 (9). The structures were refined with atomic scattering factors, corrected for anomalous dispersion, as provided by that program. The weighting schemes accounted for the counting statistics, and a parameter correcting for isotropic second-

ary extinction was optimized for each data set during the least-squares refinements. To check for the correct compositions we also refined the occupancy parameters of all atomic positions together with anisotropic thermal parameters and with fixed scale factors. No significant deviations from the ideal occupancy values were observed (Table 3), and in subsequent least-squares cycles the ideal occupancy values were used.

The displacement parameters of the Zn2, Cd2, and P2 positions turned out to be rather high. A similar difficulty

TABLE 3
Atomic Parameters for $PrZn_3P_3$ and $PrCd_3P_3$

Atom	Position	Occupancy	x	y	z	B_{eq}[a]
		$PrZn_3P_3$ (space group $P6_3/mmc$)				
Pr	2a	1.02(1)	0	0	0	0.47(3)
Zn1	4f	0.97(2)	1/3	2/3	0.1312(1)	0.86(5)
Zn2	2d	1.00(4)	1/3	2/3	3/4	4.0(2)
P1	4f	0.90(4)	1/3	2/3	0.5870(3)	0.65(8)
P2	2c	1.13(8)	1/3	2/3	1/4	3.4(4)
		$PrCd_3P_3$ (space group $P6_3/mmc$)				
Pr	2a	0.995(5)	0	0	0	0.60(1)
Cd1	4f	1.005(5)	1/3	2/3	0.12724(2)	0.99(1)
Cd2	2d	0.997(6)	1/3	2/3	3/4	2.48(2)
P1	4f	0.99(1)	1/3	2/3	0.57775(8)	0.62(2)
P2	2c	1.01(2)	1/3	2/3	1/4	1.45(4)

[a] The equivalent isotropic displacement parameters B_{eq} are in units of 10^4 pm^2. For the results of the refinements of the atomic sites Zn2, Cd2, and P2 with split positions see text. The occupancy values were obtained in separate least-squares cycles. In the final refinement cycles the ideal occupancy values were resumed.

TABLE 4
Anisotropic Displacement Parameters (pm²) of PrZn₃P₃ and PrCd₃P₃[a]

	$U_{11} = U_{22}$	U_{33}	U_{12}
	PrZn₃P₃		
Pr	43(4)	92(7)	22(2)
Zn1	117(8)	93(13)	58(4)
Zn2	565(38)	382(49)	283(19)
P1	82(15)	83(24)	41(7)
P2	615(77)	65(55)	308(39)
	PrCd₃P₃		
Pr	70(1)	88(2)	35(1)
Cd1	142(2)	93(2)	71(1)
Cd2	238(3)	467(7)	119(1)
P1	68(4)	100(7)	34(2)
P2	236(9)	77(11)	118(4)

[a] The displacement parameters U_{13} and U_{23} equal zero for symmetry reasons.

had been encountered during the structure refinements of ScAl₃C₃ and UAl₃C₃ (7, 8). However, in the structures of these carbides only one aluminum site had a large U_{33} parameter, and there the refinements with a splitting of this aluminum position resulted in an acceptable result assuming the space group $P6_3/mmc$. Nevertheless, the correct space group for the carbides was considered to be $P6_3mc$, where refinements with full occupancy of all atomic sites, assuming twinning, resulted in comparable displacement parameters for all atoms (7). In the present case the situation is more complicated, since not only the U_{33} parameter of the Zn2 and Cd2 sites, but also the U_{11} parameters of these and the P2 sites are rather high (Table 4). It was possible to refine split positions for the Zn2 and Cd2 atoms in space group $P6_3/mmc$, assuming they occupy the Wyckoff positions $12k$ and $4f$ with occupancy values of 1/6 and 1/2, respectively, and assuming isotropic displacement parameters. Similarly, split positions were also introduced for the P2 atoms of both structures with the Wyckoff position $6h$ and an occupancy parameter of 1/3. These refinements resulted in similar residuals as obtained before with unsplit positions and anisotropic displacement parameters. In reality, one should assume these structures with disordered split atomic positions to have at least short-range order (possibly dynamic) with full occupancy of atomic sites in a lower symmetry space group. However, there are many possibilities for the loss of rotational and/or translational symmetry (10 and references therein) and we did not attempt to refine these structures in lower symmetry space groups, assuming our crystals to be twinned. As can be seen from Fig. 1, the split atomic positions are not located that far away from the fully occupied ideal positions and we therefore preferred to consider the refinements with full occupancy of the atomic sites and anisotropic displacement parameters as the
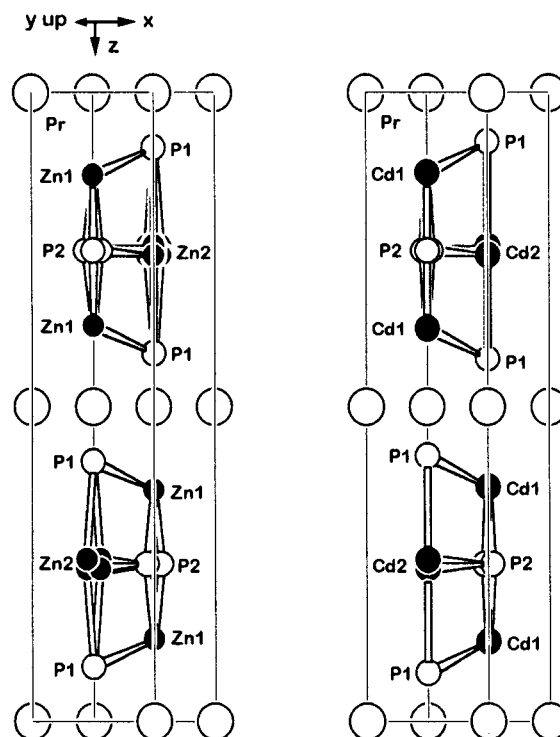

FIG. 1. The hexagonal crystal structures of PrZn₃P₃ and PrCd₃P₃ as refined with split atomic positions for those atoms showing large anisotropic displacement parameters (11).

final refinements. The results of these refinements and the interatomic distances are summarized in Tables 2–5. The results of the refinements with split atomic positions and the structure factor tables are available (11).

TABLE 5
Interatomic Distances in PrZn₃P₃ and PrCd₃P₃[a]

Pr:	6P1	290.8/295.1
	6Zn1/Cd1	350.8/362.5
Zn1/Cd1:	1P2	237.4/256.7
	3P1	249.4/267.1
	3Zn2/Cd2	332.8/355.7
	3Pr	350.8/362.5
Zn2/Cd2:	3P2	233.2/246.2
	2P1	325.7/360.1
	6Zn1/Cd1	332.8/355.7
P1:	3Zn1/Cd1	249.4/267.1
	3Pr	290.8/295.1
	1Zn2/Cd2	325.7/360.1
P2:	3Zn2/Cd2	233.2/246.2
	2Zn1/Cd1	237.4/256.6

[a] The distances were calculated using the lattice constants obtained from the powder data (Table 1). All distances shorter than 400 pm are listed. The standard deviations are all 0.6 pm and 0.2 pm or less for PrZn₃P₃ and PrCd₃P₃, respectively.
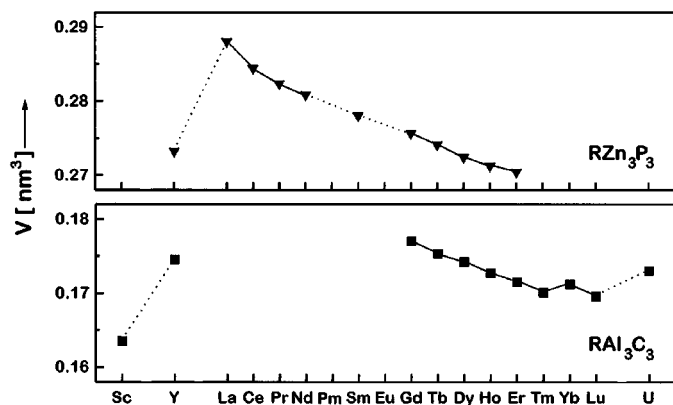
FIG. 2. Cell volumes of the new phosphides RZn_3P_3 (R = Y, La–Nd, Sm, Gd–Er). To facilitate comparisons, the cell volumes of the corresponding $ScAl_3C_3$ type carbides RAl_3C_3 (R = Sc, Y, La–Nd, Sm, Gd–Lu, U) are also given.

DISCUSSION

The new zinc-containing phosphides are represented by their cell volumes in Fig. 2 together with the (nearly) isotypic $ScAl_3C_3$-type carbides RAl_3C_3 (6–8). The structure of these carbides may be considered as practically isotypic, since it can be refined in the same space group as the structure of $PrZn_3P_3$ and $PrCd_3P_3$ ($P6_3/mmc$), although the refinements of the carbide structure in the lower symmetry space group $P6_3mc$ is more satisfactory (7), as already discussed above. The fact that the phosphides RZn_3P_3 and $PrCd_3P_3$ are almost isotypic with the carbides RAl_3C_3 is somewhat surprising, since the carbon atoms are much smaller than the phosphorus atoms, and to our knowledge no ternary isotypic carbides and phosphides have been reported. However, several binary carbides of transition elements with the composition TC and the phosphides of the rare earth
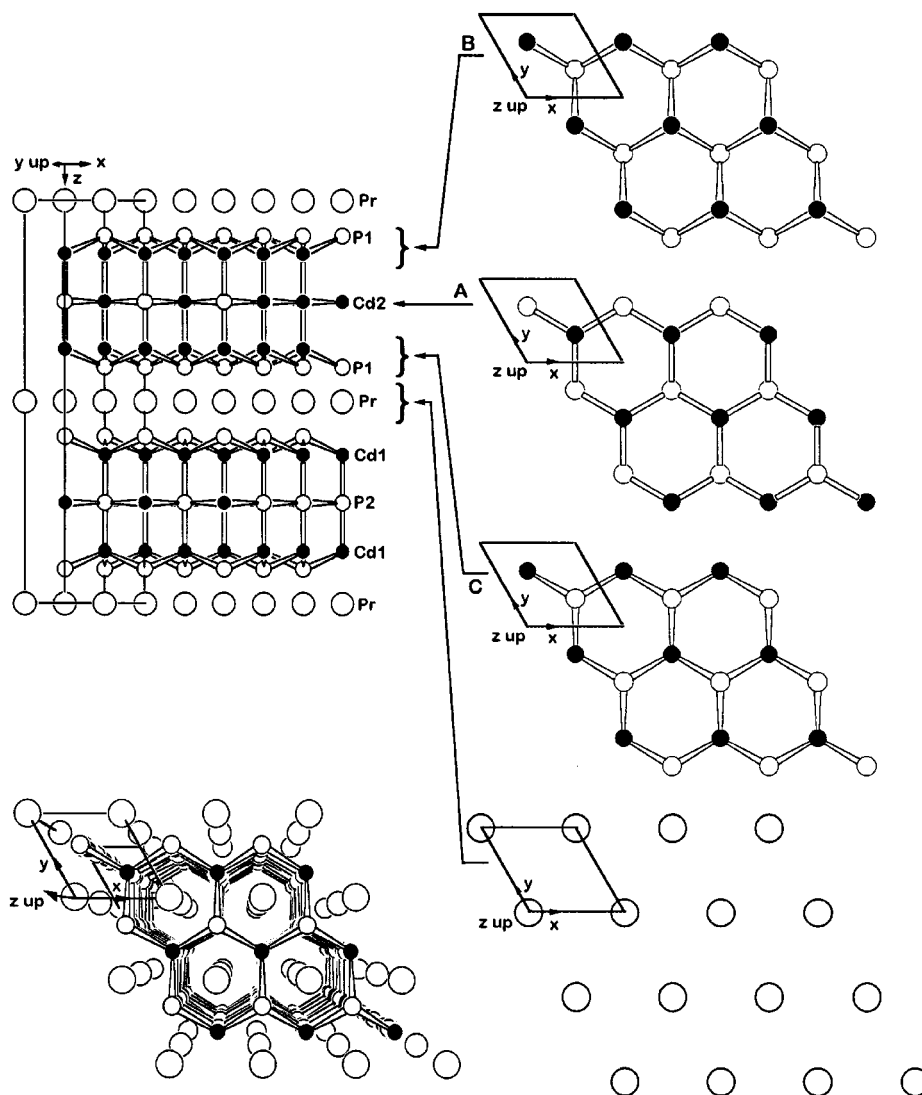

FIG. 3. Structure of $PrCd_3P_3$. The Pr and CdP layers are indicated; in the right-hand parts of the figure they are projected along directions perpendicular to the layers. The lower part of the figure shows a perspective view of the structure.

elements LnP are isotypic, both crystallizing with NaCl-type structure (12).

The recently reported compound $SmZn_3P_3$ (4) is completely isotypic with the structures reported here for $PrZn_3P_3$ and $PrCd_3P_3$, although the structure of $SmZn_3P_3$ had been reported for the space group $P6_322$. The special atomic positions occupied in this structure are the same for both space groups. However, since the space group $P6_322$ is of lower symmetry than the space group $P6_3/mmc$, the latter group is correct, at least for the average structure as discussed above. Again, large isotropic displacement parameters had been found for the twofold zinc and phosphorus positions of $SmZn_3P_3$. Optical reflectance spectra of this phosphide had indicated a band gap of 0.60 eV (4). Hence, semiconductivity may also be assumed for the isotypic compounds reported here.

The cerium atoms in $CeZn_3P_3$ are trivalent, as can be concluded from the cell volume of this compound, which fits smoothly between the cell volumes of $LaZn_3P_3$ and $PrZn_3P_3$ (Fig. 2). In contrast, in combination with phosphorus the cerium atoms are sometimes tetravalent or frequently they have mixed or intermediate valence, as can be seen from similar cell volume plots of phosphides with $Zr_2Fe_{12}P_7$ (13) and $LaFe_4P_{12}$ type structures (14).

The structure of the isotypic compounds RZn_3P_3 and $PrCd_3P_3$ is shown in Fig. 3, with the cadmium compound as a representative. The cadmium and the phosphorus atoms form hexagonal nets, wherein the cadmium and phosphorus atoms alternate. In the description of this structure with the space group $P6_3/mmc$, the net designated with the letter **A** is flat, similar to the nets in the hexagonal modification of boron nitride BN; in reality this net may be sligthly (possibly dynamically) puckered as is indicated in Fig. 1. Above and below this net **A** are the nets **B** and **C**. These nets are strongly puckered with all six-membered rings in chair conformation, as is known for example from the wurtzite structure of ZnS. In the flat net **A** the Cd2 and P2 atoms have three close neighbors of the other kind within their net with Cd–P distances of 246.2 pm. In the case of the P2 atoms this coordination is augmented by two Cd1 atoms from the nets above and below (Fig. 4) with P2–Cd1 distances of 256.6 pm. In the case of the Cd2 atoms the triangular P2 coordination is augmented by two more phosphorus atoms (P1) of the neighboring nets with the rather large Cd2–P1 distance of 360.1 pm. This distance is even greater than the distance (of 355.7 pm) of the central Cd2 atom to the six Cd1 atoms belonging to the nets **B** and **C** above and below. Hence, the Cd2 atoms have essentially only three close (P2) neighbors, and this is the reason for their large U_{33} displacement parameter. The Cd1 atoms of the outer nets (nets **B** and **C** of Fig. 3) have tetrahedral phosphorus coordination with Cd–P distances of 256.7 pm $(1 \times)$ and 267.1 pm $(3 \times)$, while the P1 atoms of these outer nets have three cadmium neighbors within their nets; in
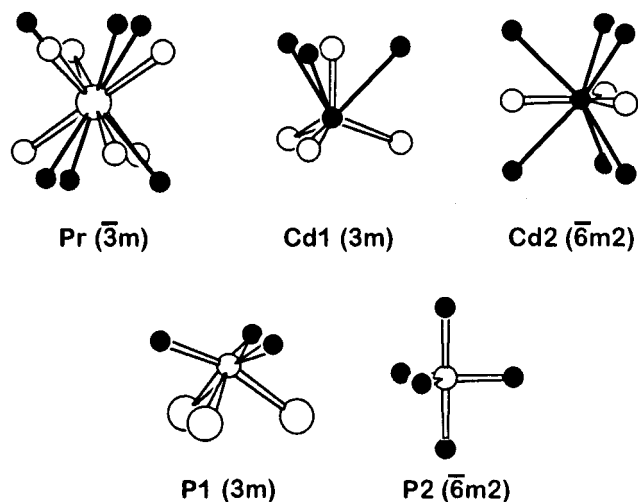

FIG. 4. Near-neighbor coordinations in $PrCd_3P_3$. The site symmetries are indicated in parentheses.

addition they are coordinated by three praseodymium atoms.

The praseodymium atoms form layers separating the cadmium–phosphorus nets. They are coordinated by six P1 atoms at 295.1 pm in octahedral arrangement. Six more Cd1 atoms outside two of the eight triangular faces of the PrP_6 octahedra with Pr–Cd1 distances of 362.5 pm can hardly be counted as neighbors.

We have recently reported on the two series of rare earth zinc phosphide oxides and arsenide oxides $RZnPO$ and $RZnAsO$ (3). They crystallize with two structure types. The one, determined for NdZnAsO is a tetragonal layer structure, which has similarities with the tetragonal layer structure found for $Pr_3Zn_2As_6$ (1). The other one, which was determined for NdZnPO, is hexagonal and may be considered as consisting of two kinds of double layers of the compositions NdO and ZnP. The double layers with the composition ZnP of NdZnPO are very similar to the triple-layer CdP of the presently reported compound $PrCd_3P_3$.

Another way of looking at the structure of $PrCd_3P_3$ is that of close-packed spheres. The large praseodymium and cadmium atoms each form close-packed layers, which are stacked in the sequence $ABCBACBC$ corresponding to PrCdCdCdPrCdCdCd (Fig. 5). Using the Jagodzinski–Wyckoff notation the stacking may also be described with the sequence $cchccchc$, i.e., $(hccc)_2$, where the layers correspond to the atom sequence $(CdCdPrCd)_2$. The phosporus atoms P1 occupy octahedral voids between two adjacent c layers and the P2 atoms occupy trigonal bipyramidal voids with their centers situated in the h layers.

Chemical bonding in $PrCd_3P_3$ may be rationalized to a first approximation by simple concepts with the formulas $Pr^{3+}(Cd_3P_3)^{3-}$ and $Pr^{3+}(Cd^{2+})_3(P^{3-})_3$, where the superscripts represent oxidation numbers (formal charges). These
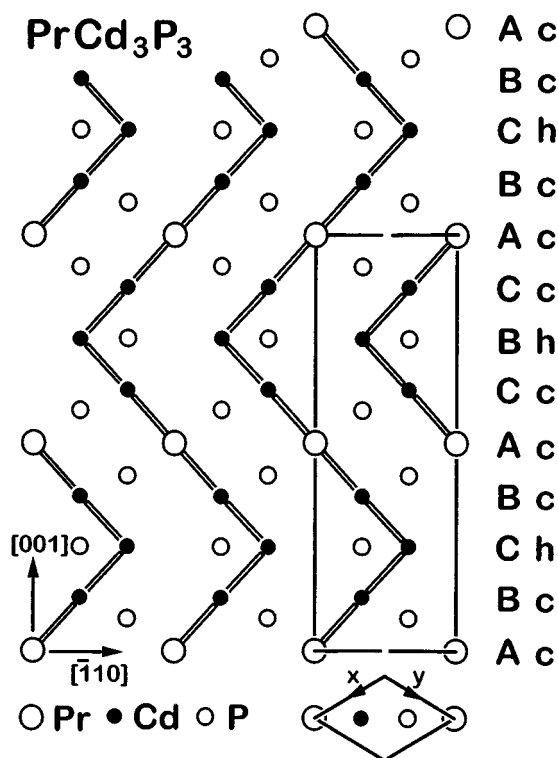
FIG. 5. Stacking sequence of the praseodymium and cadmium atoms in the structure of $PrCd_3P_3$. The metal atoms of adjacent layers are connected by zigzag lines. The phosphorus atoms are located at interstitial sites. At the right-hand part of the figure the stacking sequence of the metal atoms is symbolized using the *ABC* and the Jagodzinski–Wyckoff notations.

formulas account for the fact that the phosphorus atoms do not form any P–P bonds. Since the phosphorus atoms are the most electronegative components of the compound they can be assumed to fully use their $3s$ and $3p$ orbitals for more or less covalent bonding toward the cadmium and praseodymium atoms (octet rule). In the formulas given above, these electrons are counted at the phosphorus atoms. Hereby the praseodymium and cadmium atoms obtain their usual oxidation numbers. In agreement with this rationalization, the nearly isotypic rare earth aluminum carbides RAl_3C_3 mentioned above can be rationalized by the analogous electron counting formula $R^{3+}(Al^{3+})_3(C^{4-})_3$.

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