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The Arsenides $LnPd_3As_2$ (Ln = La–Nd, Sm, Gd) and Structure Refinement of $CePd_{2-x}As_2$ with the $ThCr_2Si_2$ Structure

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The title compounds were prepared in well-crystallized form by annealing the corresponding binary arsenides in a NaCl/KCl flux. The compounds $LnPd_3As_2$ crystallize with a new monoclinic structure type, which was determined from single-crystal X-ray data of $GdPd_3As_2$: $C2/m$, a = 1656.3(6) pm, b = 404.6(2) pm, c = 993.7(4) pm, β = 107.85(2)°, Z = 6, R = 0.025 for 1728 structure factors and 58 variable parameters. These arsenides belong to a large structural family with a metal to metalloid ratio of 2:1. Somewhat unusual features in the structure of $GdPd_3As_2$ are the (distorted) octahedral coordination of one gadolinium site and the square-planar coordination of arsenic atoms around two palladium sites. All of these, however, are also observed for the corresponding atoms in the previously reported, closely related structure of $Th_5Fe_{19}P_{12}$. $CePd_{2-x}As_2$ has the tetragonal $ThCr_2Si_2$ structure (a = 425.1(2) pm, c = 1026.1(6)pm, R = 0.023 for 244 F values and 11 variables) with an As–As distance of 247.1(1) pm. The refinement of the occupancy parameter of the palladium position resulted in a value of 87.9(2)% corresponding to the formula $CePd_{1.758(4)}As_2$. It is argued that the formation of these defects reduces antibonding (destabilizing) Pd–Pd interactions.

INTRODUCTION

Ternary lanthanoid-transition-metal phosphides have been investigated extensively in the past (1–12). Especially those with $ThCr_2Si_2$ and $CaBe_2Ge_2$ type structure are well characterized (8, 13–17). Much less is known about the corresponding arsenides (7, 18). Here we report about a new series of ternary arsenides and about a structure refinement of $CePd_{2-x}As_2$. The lattice constants of the latter compound were reported earlier (19) and some preliminary results on the crystal structure of $GdPd_3As_2$ are also available (20).

SYNTHESIS

Starting materials were the elemental components; the metals with nominal purities >99.9%. Arsenic (99%) was further purified twice by fractional sublimation. Filings of the rare earth metals were prepared from ingots and stored under dried paraffin oil. This was washed away by dried n-hexane prior to the reactions and the hexane was evaporated under high vacuum. First the binary arsenides LnAs were prepared by annealing the components in evacuated, sealed silica tubes at 500°C for 3 days. Then these arsenides were mixed with palladium powder and additional arsenic in the ratio LnAs:Pd:As = 1:3:1. Cold-pressed pellets of these mixtures were annealed in evacuated, sealed silica tubes for 2 days at 500°C and subsequently for about 6 days at 800°C.

The single crystal of $GdPd_3As_2$ used for the structure determination was isolated form a sample, where powders of the binary arsenides GdAs and β-Pd_2As (21) were reacted in a NaCl/KCl (1:1) flux for 5 weeks at temperatures between 700 and 800°C. The ratio sample weight:flux weight was 1:5. This method also was used to prepare a well-crystallized sample of $CePd_{2-x}As_2$ with similar reaction conditions. The flux was dissolved in water. This treatment does not visibly attack the ternary arsenides. Energy dispersive analyses of the products in a scanning electron microscope did not show any impurity elements with atomic numbers greater than 11 (sodium).

LATTICE CONSTANTS

The samples were characterized through their Guinier powder patterns recorded with Cu$K\alpha_1$ radiation. The lattice constants were refined by least-squares fits of the data using α-quartz (a = 491.30 pm, c = 540.46 pm) as a standard. To ensure proper indexing, the observed powder patterns were compared with those calculated, assuming the positional parameters obtained during the structure refinements. The lattice constants for the arsenides $LnPd_3As_2$ are listed in Table 1. Those obtained for the tetragonal $ThCr_2Si_2$ type compound $CePd_{2-x}As_2$ (Table 2) were in good agreement with the ones reported earlier (a = 426.8(2) pm, c = 1027.3(1) pm) (19).

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TABLE 1
Lattice Constants of the Monoclinic Arsenides $LnPd_3As_2$ (Ln = La–Nd, Sm, Gd)[a]

Compound	a (pm)	b (pm)	c (pm)	β (°)	V (nm^3)
$LaPd_3As_2$	1669.8(9)	415.0(2)	1000.3(4)	108.12(2)	0.6587
$CePd_3As_2$	1666.7(8)	412.2(2)	999.4(4)	108.05(4)	0.6527
$PrPd_3As_2$	1665.1(9)	410.0(3)	996.6(8)	108.01(8)	0.6470
$NdPd_3As_2$	1660.1(6)	409.1(2)	995.4(4)	108.00(4)	0.6430
$SmPd_3As_2$	1657.8(8)	406.1(2)	994.5(4)	107.97(4)	0.6371
$GdPd_3As_2$	1656.3(6)	404.6(2)	993.7(4)	107.85(2)	0.6339

[a] Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

TABLE 3
Atom Parameters of $GdPd_3As_2$[a]

Atom	$C2/m$	x	y	z	B_{eq}
Gd1	4*i*	0.15510(2)	0	0.70148(3)	0.584(4)
Gd2	2*a*	0	0	0	0.728(6)
Pd1	4*i*	0.04303(3)	0	0.33132(5)	0.606(6)
Pd2	4*i*	0.22125(3)	0	0.39087(5)	0.693(6)
Pd3	4*i*	0.31977(3)	0	0.03300(5)	0.751(6)
Pd4	4*i*	0.62178(3)	0	0.19830(5)	0.731(6)
Pd5	2*d*	0	1/2	1/2	0.773(9)
As1	4*i*	0.19914(4)	0	0.13199(6)	0.564(8)
As2	4*i*	0.36388(4)	0	0.54501(6)	0.476(8)
As3	4*i*	0.46029(4)	0	0.21324(7)	0.556(8)

[a] The last column contains the equivalent isotropic thermal parameters $\times 100$, in units of nm^2.

STRUCTURE REFINEMENTS

Single crystals of $GdPd_3As_2$ were investigated in a Weissenberg camera with Cu$K\alpha$ radiation. They showed monoclinic symmetry and systematic extinctions, which led to the space groups $C2/m$, $C2$ and Cm of which $C2/m$ was found to be correct during the structure refinements. The intensity data for the structure determinations of $GdPd_3As_2$ and $CePd_{2-x}As_2$ were recorded on an automated four-circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. The background was determined at both ends of each $\theta/2\theta$ scan. Empirical absorp-

TABLE 2
Crystal Data of $GdPd_3As_2$ and $CePd_{2-x}As_2$

	$GdPd_3As_2$	$CePd_{2-x}As_2$
Space group	$C2/m$ (No. 12)	$I4/mmm$ (No. 139)
Lattice constants (single-crystal diffractometer)		
a (pm)	1651.4(3)	424.0(2)
b (pm)	403.7(1)	
c (pm)	991.3(2)	1024.6(5)
β (°)	107.88(2)	
V (nm^3)	0.6289	0.1842
Lattice constants (Guinier powder)[a]		
a (pm)	1656.3(6)	425.1(2)
b (pm)	404.6(2)	
c (pm)	993.7(4)	1026.1(6)
β (°)	107.85(2)	
V (nm^3)	0.6339	0.1853
Formula weight	626.3	477.2[b]
Formula units/cell,	$Z = 6$	$Z = 2$
Calculated density (g/cm^3)	9.84	8.55[b]
Crystal dimensions (mm^3)	0.02 × 0.03 × 0.25	0.07 × 0.09 × 0.13
$\theta/2\theta$ scans up to	$2\theta = 75°$	$2\theta = 90°$
Range in h, k, l	±28, 0 − 7, ±17	±8, ±8, ±20
Total no. of reflections	4280	3056
Unique reflections	2143	261
Inner residual	$R_i = 0.015$	$R_i = 0.033$
Reflections with $I_o > 3\sigma(I_o)$	1728	244
Number of variables	58	11
Conventional residual	$R = 0.025$	$R = 0.023$
Weighted residual	$R_w = 0.032$	$R_w = 0.034$

[a] The lattice constants obtained from single-crystal diffractometer data are usually affected by systematic errors due to absorption. Therefore the interatomic distances were calculated with the lattice constants form the powder data.

[b] For the formula $CePd_{1.76}As_2$.

TABLE 4
Atom Parameters of $CePd_{2-x}As_2$[a]

Atom	*I4/mmm*	Occupancy	*x*	*y*	*z*	$B_{11} = B_{22}$	B_{33}	B_{eq}
Ce	2(*a*)	1	0	0	0	0.370(6)	0.279(8)	0.339(3)
Pd	4(*d*)	0.879(2)	0	1/2	1/4	0.854(9)	0.79(1)	0.833(4)
As	4(*e*)	0.979(3)	0	0	0.37961(6)	1.17(1)	0.29(2)	0.876(6)

[a] The anisotropic thermal parameters B (×100, in units of nm^2) are defined by $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33})]$. The values of B_{12}, B_{13}, and B_{23} equal zero for symmetry reasons in this structure.

tion corrections were made from psi-scan data. Further details of the data collections are summarized in Table 3.

The structure of $GdPd_3As_2$ was solved by direct methods (22), which resulted in the positions of nine atoms. A 10th position was found by a difference Fourier synthesis. A full-matrix least-squares program was used to refine both structures. The atomic scattering factors (23) were corrected for anomalous dispersion (24). The weighting schemes included a term which accounted for the counting statistics, and a factor which corrected for isotropic secondary extinction was fitted as a least-squares parameter. To check for deviations from the ideal compositions the occupancy parameters were refined together with the thermal parameters. For the $GdPd_3As_2$ structure these values varied between 99.1(2)% for Pd5 and 100.9(1)% for Gd2 except for the Pd3 position, where an occupancy of 97.8(2)% was obtained. Nevertheless, the ideal occupancy values were assumed again for all positions during the final least-squares cycles. For $CePd_{2-x}As_2$, however, a substantial deviation from the full occupancy was obtained for the Pd position and during the final least-squares cycles only the occupancy of the Ce position was assumed to be ideal, to hold the scale factor. The final residuals, atomic parameters, and interatomic distances are listed in Tables 2–6.

DISCUSSION

The $GdPd_3As_2$ type arsenides reported here crystallize with a new structure type (Fig. 1), which belongs to a large structural family of phosphides, silicides, and homologues with a metal to metalloid ratio of 2 : 1. The metalloid atoms (P, Si) of these compounds are situated in trigonal prisms formed by the metal atoms, and the coordination number (CN) of the metalloid atoms is usually increased to nine by three additional metal atoms outside the rectangular faces of the prisms. In most of these structures all atoms are situated on two mirror planes, which extend perpendicular to the short axis, and this axis usually corresponds to the parallel edges of the trigonal prisms around the metalloid atoms. The trigonal prisms are linked with each other by common edges (Fig. 2) and in addition by the two trigonal faces, thus forming infinte pillars, which extend

TABLE 5
Interatomic Distances in $GdPd_3As_2$[a]

Gd1–2	As3	307.5	Pd4–1	As2	248.8
2	As2	311.7	2	As1	258.6
2	As1	319.5	1	As3	272.4
1	Pd1	319.7	1	Pd3	275.4
2	Pd2	320.6	2	Pd2	292.2
2	Pd3	324.9	2	Pd1	293.2
2	Pd5	339.8	2	Gd2	310.0
1	Pd4	352.0	1	Gd1	352.0
1	Pd3	357.5	Pd5–2	As2	242.9
1	Pd1	357.6	2	As3	272.1
1	Pd2	357.8	4	Pd1	285.4
Gd2–4	As3	314.2	4	Gd1	339.8
2	As1	315.4	As1–1	Pd3	248.3
4	Pd4	310.0	1	Pd2	248.5
2	Pd1	314.8	2	Pd3	256.2
4	Pd3	370.3	2	Pd4	258.6
Pd1–2	As3	252.2	1	Gd2	315.4
2	As2	261.1	2	Gd1	319.4
1	Pd2	282.7	(1	Pd1	370.8)
2	Pd5	285.4	As2–1	Pd2	238.9
2	Pd4	293.2	1	Pd5	242.9
1	Gd2	314.8	1	Pd4	248.8
1	Gd1	319.7	2	Pd1	261.1
1	Gd1	357.6	2	Pd2	265.3
(1	As1	370.8)	2	Gd1	311.7
Pd2–1	As2	238.9	1	As3	315.7
1	As1	248.5	As3–1	Pd3	246.4
2	As2	265.3	2	Pd1	252.2
1	Pd1	282.7	1	Pd5	272.1
2	Pd2	290.5	1	Pd4	272.4
2	Pd4	292.2	2	Gd1	307.5
2	Gd1	320.6	2	Gd2	314.2
1	Gd1	357.8	1	As2	315.7
Pd3–1	As3	246.4			
1	As1	248.3			
2	As1	256.2			
1	Pd4	275.4			
2	Pd3	298.9			
2	Gd1	324.9			
1	Gd1	357.5			
2	Gd3	370.3			

[a] All distances shorter than 400 pm (Gd) and 385 pm (Pd, As) are listed. These distances correspond to the coordination polyhedra of Fig. 1 with the exception of the Pd1–As1 distance of 370.8 pm. The standard deviations computed from those of the positional parameters and the lattice constants are all equal to or less than 0.2 pm.

TABLE 6
Interatomic Distances in $CePd_{2-x}As_2$[a]

Ce–8 As	325.0	As–1 As	247.1
8 Pd	333.1	4 Pd	250.7
Pd–4 As	250.7	4 Ce	325.0
4 Pd	300.6		
4 Ce	333.1		

[a] The standard deviations result essentially only from those of the lattice constants. They are 0.2 pm or less.

along the short axis. Of the reports already cited above, many (2–7, 11, 12) describe structures which belong to this large structural family. Frequently they are classified by the way the trigonal prisms are linked with each other (26–30).

In $GdPd_3As_2$ there are two kinds of gadolinium atoms. The Gd1 atoms have trigonal prismatic arsenic coordination, and the Gd2 atoms are situated in a distorted octahedron of arsenic atoms. While the trigonal prismatic metalloid coordination is frequently found for the large electropositive metal atoms, the distorted octahedral coordination is rare. It was, however, observed before for the dysprosium atoms in $DyNi_4As_2$ with $ZrFe_4Si_2$ type structure (7) and for one thorium site in $Th_5Fe_{19}P_{12}$ (25). In addition to the arsenic atoms the gadolinium atoms of $GdPd_3As_2$ have 11 and 10 palladium neighbors, respectively, at distances ranging between 310 and 370 pm. At least those with the shorter distances might be considered as bonding interactions. Both gadolinium atoms have two gadolinium neighbors at a distance corresponding to the short translation period (404.6 pm). These gadolinium neighbors might be counted as belonging to the coordination polyhedra for geometric reasons, although Gd–Gd interactions at this distance can only be very weak.

All palladium atoms have four arsenic neighbors at distances covering the range from 238.9 to 272.4 pm. These arsenic atoms are forming distorted tetrahedra in the case of Pd2, Pd3, and Pd4. The tetrahedral coordination occurs most frequently for the late transition metal atoms in this structural family, while the (distorted) quadratic arsenic coordination of the Pd1 and Pd5 atoms is rarely found in such compounds. Again the closely related structure of $Th_5Fe_{19}P_{12}$ provides two more examples for a quadratic transition metal coordination with the Fe8 and Fe10 coordinations of that compound (25). In addition to the arsenic atoms each palladium atom has between three and five palladium neighbors at distances from 275.4 to 298.9 pm, and also between three and five gadolinium neighbors at

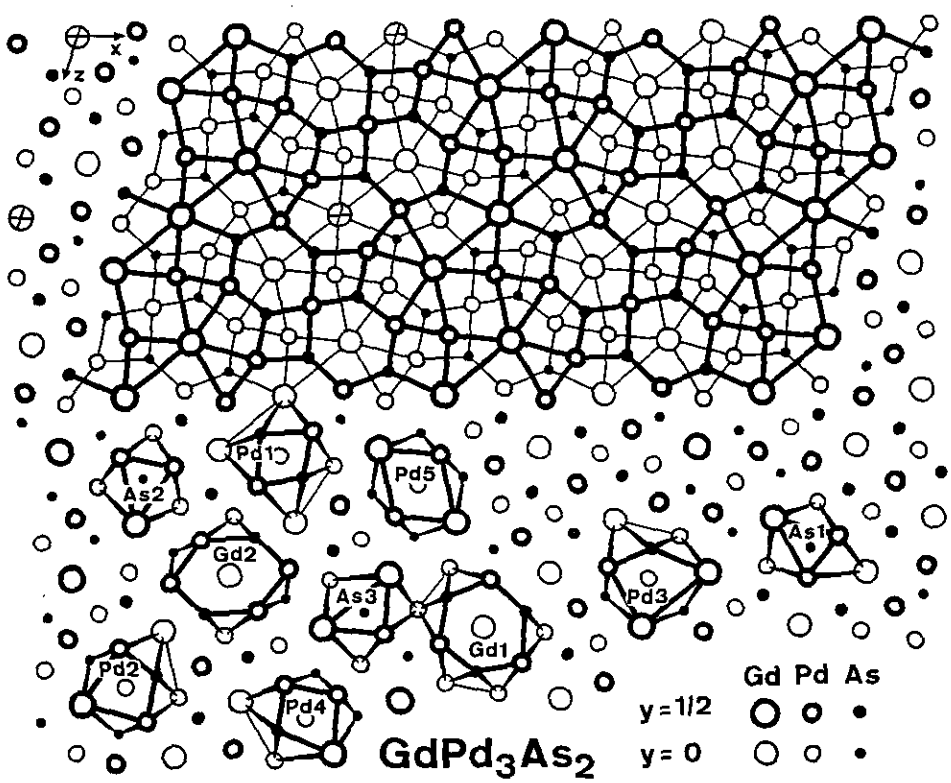

FIG. 1. Crystal structure and coordination polyhedra of $GdPd_3As_2$. In the upper part of the drawing, atoms connected by thick and thin lines are separated by half a translation period of the projection direction. These lines are drawn to facilitate a visualization of the structure; they do not necessarily correspond to chemical bonds.

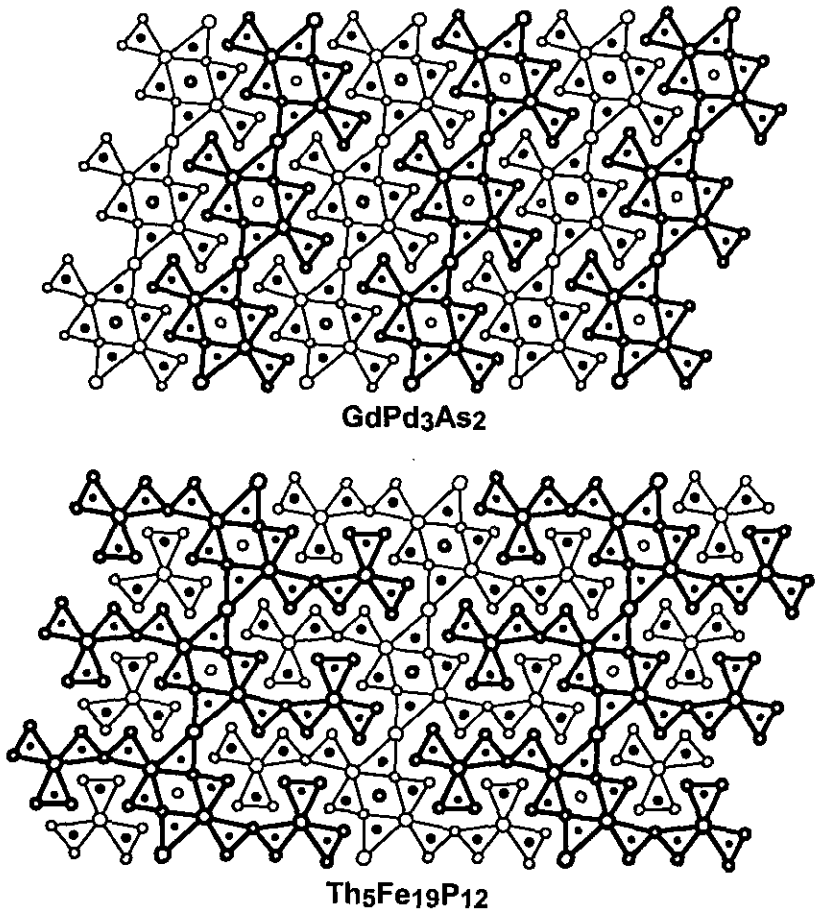

FIG. 2. The linking of the trigonal metal prisms around the arsenic atoms in $GdPd_3As_2$ and the closely related structure of $Th_5Fe_{19}P_{12}$ (25). Atoms connected by heavy and light lines are separated from each other by half a translation period of the projection direction. Large open circles represent the gadolinium and thorium atoms; the iron and palladium atoms are shown as small circles.

distances between 310.0 and 370.3 pm. With these additional metal neighbors each palladium atom attains the coordination number 12.

The arsenic atoms all have CN 9; a tricapped trigonal prism of metal atoms, and this is the usual coordination for the metalloid atoms in this structural family as already mentioned above. Since the arsenic atoms are the most electronegative component of the compound and since there are no As–As bonds, the arsenic atoms obtain the oxidation number −3. The gadolinium atoms on the other hand, as the most electropositive component of the compound obtain the oxidation number +3. Thus, the compound may be written with the formula $(6\ Gd^{3+})^{18+}(18\ Pd)^{18+}(12\ As^{3-})^{36-}$ and therefore the 18 palladium atoms obtain 18 positive formal charges, and one may ask how these are distributed among the 18 palladium atoms. Although there is no need to assign integral oxidation numbers in a solid state compound with a band structure, most palladium atoms will probably be close to +1, since there are no great differences between the average Pd–As distances of the palladium atoms with quadratic (Pd1–As: 256.7 pm; Pd5–As: 257.5 pm) and tetrahedral arsenic coordination (Pd2–As: 254.5 pm; Pd3–As: 251.8 pm; Pd4–As 259.6 pm). Certainly there is also some Pd–Pd bonding. This can be concluded from the fact that the shortest average Pd–As distance occurs for the Pd3 atom, which has the smallest number of Pd neighbors (three), while the other have four or five.

The refinement of the $ThCr_2Si_2$ type structure of $CePd_{2-x}As_2$ resulted in an occupancy parameter for the palladium position of only 87.9% with a standard deviation of 0.2%. This corresponds to the formula $CePd_{1.758(4)}As_2$ (disregarding the much smaller number of defects on the arsenic site). Similar deviations from the ideal composition may be assumed for the other arsenides $LnPd_{2-x}As_2$ with $ThCr_2Si_2$ type structure (19). In the homologous arsenide $NdNi_2As_2$ (31) with the closely related primitive tetragonal $CaBe_2Ge_2$ type structure half of the transition metal sites are occupied by arsenic atoms. For that reason one could argue that a portion of the palladium atoms in $CePd_{2-x}As_2$ are substituted by the lighter arsenic atoms. However, this is not very probable in view of the fact

that an even larger number of defects were found in $EuNi_{1.53}Sb_2$ with $ThCr_2Si_2$ type structure (32), and there the antimony atoms are the components with the higher scattering power. Other reasons why the transition metal sites may not be fully occupied in $ThCr_2Si_2$ type pnictides of the late transition metals were discussed previously to rationalize the defects in $EuNi_{1.88}P_{1.92}$ (31).

The arsenic atoms in $CePd_{2-x}As_2$ form pairs with an As–As distance of 247.1 pm, which is close to the bond distance of 251.7 pm in both well-characterized modifications of arsenic (33). Therefore the arsenic atoms may be ascribed the oxidation number −2, and the compound may be written with the formula $Ce^{3+}(Pd_{2-x})^{1+}(As_2)^{4-}$, since the cell volume plot for the lanthanoid palladium arsenides $LnPd_2As_2$ suggests cerium is trivalent in these compounds (19). The palladium atoms have tetrahedral arsenic coordination; however, the Pd–As distances (250.7 pm) are slightly shorter than in $GdPd_3As_2$, while the Pd–Pd distances of 300.6 pm are greater than even the greatest bonding Pd–Pd distance of the gadolinium compound.

Chemical bonding in $ThCr_2Si_2$ type compounds was analyzed before, both by systematic trends of interatomic distances (19, 31, 32, 34–36) and by extended Hückel calculations (37, 38). Defects at the sites of the transition metal atoms were observed first for the phosphides $CaNi_{1.95}P_2$, $CaCu_{1.75}P_2$, and $SrCu_{1.75}P_2$ (39). The phosphorus atoms in these compounds form pairs with P–P distances of 229.7(7), 225.1(6), and 229.7(5) pm, respectively. Thus, the bonding situation in these compounds is similar to that of $CePd_{1.76}As_2$ with an As–As bond distance of 247.1(1) pm. Apparently the tendency for the formation of defects increases with the electron count of the transition metal (T) pnictogen polyanion. It was pointed out previously (36) that the formation of such defects reduces antibonding (destablizing) T–T interactions. Introducting defects allows the transfer of electrons from the T–T antibonding band to nonbonding orbitals of the transition metal and pnictogen atoms surrounding the vacant site.

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