Dimorphic $ThNi_2P_2$ with $BaCu_2S_2$ and $CaBe_2Ge_2$ Type Structure

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Two modifications of $ThNi_2P_2$ were prepared in a tin flux at 850 °C (α-$ThNi_2P_2$) and 1000 °C (β-$ThNi_2P_2$). The crystal structures of both modifications were refined from single-crystal X-ray data. α-$ThNi_2P_2$ ($BaCu_2S_2$ type structure): Pnma, a = 819.69(5), b = 394.28(3), c = 981.54(7) pm, R = 0.028 for 32 variables and 654 structure factors; β-$ThNi_2P_2$ ($CaBe_2Ge_2$ type structure): P4/nmm, a = 408.5(1), c = 908.0(3) pm, R = 0.033 for 15 variable parameters and 261 F values. Although the two structures are closely related, they can be transformed into each other only by a reconstructive phase transformation. The differences and similarities of the two structures are discussed. The high temperature form has higher symmetry, a smaller number of variable positional parameters, and a tendency for higher coordination numbers.

Introduction

In recent years several ternary actinoid transition metal phosphides with the composition An:T:P = 1:2:2 (An ≡ Th, U; T ≡ Fe, Co, Ni, Cu, Ru) have been reported. UFe_2P_2 [1] and UNi_2P_2 [2, 3] have the body-centered tetragonal $ThCr_2Si_2$ structure, while $ThCo_2P_2$ [1] and UCo_2P_2 [1] adopt the closely related primitive tetragonal $CaBe_2Ge_2$ type structure. This is also the structure found by us for the high temperature (β-) modification of $ThNi_2P_2$. The compounds $ThCu_2P_2$ [4] and UCu_2P_2 [5] have hexagonal symmetry and are isotypic with Ce_2SO_2. Finally, $ThRu_2P_2$ and URu_2P_2 [6] as well as the presently reported structure of the low temperature (α-) modification of $ThNi_2P_2$ might be considered as isotypic with $BaCu_2S_2$ [7], although there are considerable differences in the positional parameters of these compounds. We have already briefly reported about the existence of α- and β-$ThNi_2P_2$ [8].

Sample Preparation

Starting materials were ingots of thorium (nominal purity 99.9%), nickel powder (100 mesh, >99.9%), small pieces of red phosphorus (Hoechst-Knapsack, "ultrapure") and granules of tin (Merck, >99.9%). Filings of thorium were prepared under dried (Na) paraffin oil. They were washed with dried cyclohexane, stored under vacuum, and were not allowed to contact air prior to the reactions. Both compounds could be prepared with the tin flux technique in sealed silica tubes as well as by annealing of the prereacted, compacted samples without tin in alumina containers under vacuum. Well developed crystals of both compounds were obtained with the starting composition Th:Ni:P:Sn = 8:13:13:66. The elemental components were sealed in evacuated silica tubes, placed vertically in a furnace and heated slowly (20 °C/h) to the reaction temperatures. The ampoules were quenched in air and the tin-rich matrix was dissolved with slightly diluted (1:1) hydrochloric acid. The low-temperature modification was observed in pure from when the samples were annealed at 850 °C for two weeks. Samples heated at 1000 °C for 10 days contained both modifications of $ThNi_2P_2$. In samples with different starting compositions the α-modification was found to be in equilibrium with Th_3P_4 [9], Ni_5P_4 [10, 11], $Th_{12}Ni_{30}P_{21}$ [8], $Th_6Ni_{20}P_{13}$ [8], and $Th_2Ni_{12}P_7$ [8], while the β-modification was found together with Th_3P_4 and $Th_{11}Ni_{25}P_{20}$ [12]. The diffraction lines in the Guinier powder patterns of the high-temperature phase were frequently slightly diffuse, indicating a small homogeneity range. Such a sample was pressed to a pellet and annealed again for three weeks at 800 °C. This treatment completely transformed the high-temperature to the low-temperature modification. Both compounds can be easily

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distinguished by their crystal shapes. α-$ThNi_2P_2$ crystallizes in the form of short needles, while single-crystals of β-$ThNi_2P_2$ are nearly equidimensional. The crystals of both forms have silvery luster, the powders are black.

The samples were characterized through their Guinier powder patterns with $CuK\alpha_1$ radiation using α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The lattice constants were refined by least-squares fits. Energy dispersive X-ray analyses of single-crystals of both modifications revealed no impurity elements heavier than sodium (detectability limit: 1 at %).

Structure Determinations

Single-crystals of both modifications of $ThNi_2P_2$ were examined with the Weissenberg method to check their symmetry and suitability for X-ray intensity data collection. The intensity measurements were carried out on a four-circle diffractometer with graphite-monochromated $MoK\alpha$ radiation, a scintillation counter with pulse-height discriminator and background counts at both ends of each $\theta/2\theta$-scan.

The crystal structure of α-$ThNi_2P_2$ was isotypic with $ThRu_2P_2$ [6] and $BaCu_2S_2$ [7] as revealed from the similarity of their Guinier powder patterns. The small primitive tetragonal cell of the β-modification suggested isotypy with UCo_2P_2 [1] and $CaBe_2Ge_2$ [13]. Both assignments turned out to be correct during the structure refinements with a full-matrix least-squares program using atomic scattering factors [14], corrected for anomalous dispersion [15]. Parameters accounting for isotropic secondary extinction were included in the refinements. Weights were assigned according to the counting statistics. Both structures were refined with anisotropic thermal parameters for all atomic sites. To check for deviations from the ideal composition both structures were also refined with variable occupancy parameters together with the thermal parameters. The occupancy parameters varied between the values of 0.956(8) for P1 and 1.022(8) for P2 in the α-modification, and between 0.99(1) for Ni1 and 1.06(2) for P2 in the β-modification. In the final least-squares cycles the ideal occupancies were assumed. The crystallographic data are summarized in the Tables I and II. The positional parameters for α-$ThNi_2P_2$ correspond

Table I. Crystal data for the low (α-) and high (β-) temperature modifications of $ThNi_2P_2$.

Compound	α-$ThNi_2P_2$		β-$ThNi_2P_2$	
Structure type	$BaCu_2S_2$		$CaBe_2Ge_2$	
Space group	Pnma (No. 62)		P4/nmm (No. 129)	
Lattice constants from Guinier powder [and single crystal] data				
a [pm]	819.69(5)	[818.0(2)]	408.5(1)	[408.0(1)]
b [pm]	394.28(3)	[393.7(1)]		
c [pm]	981.54(7)	[980.0(2)]	908.0(3)	[907.6(2)]
V [nm^3]	0.3172	[0.3156]	0.1515	[0.1511]
Formula units/cell, Z	4		2	
Formula weight	411.4		411.4	
Calculated density [g/cm^3]	8.62		9.02	
Crystal dimensions [μm^3]	20×20×100		30×30×20	
$\theta/2\theta$ scans up to	$2\theta = 70°$		$2\theta = 100°$	
Range in hkl	±13 −7 ±15		±8 ±8 ±18	
Total no. of reflections	3576		4300	
Absorption corrections for from psi scans				
Highest/lowest transmission	1.38		2.26	
Unique reflections	1006		537	
Inner residual	0.025		0.038	
Reflections with $I > 3\sigma(I)$	654		261	
Number of variables	32		15	
Conventional residual	R = 0.028		R = 0.033	
Weighted residual	R_w = 0.035		R_w = 0.041	

Table II. Atomic parameters for α-$ThNi_2P_2$ ($BaCu_2S_2$ type structure) and β-$ThNi_2P_2$ ($CaBe_2Ge_2$ type structure). The last column contains the equivalent isotropic B values of the anisotropic temperature parameters (×100, in units of nm^2).

Atom	Pnma	x	y	z	B_{eq}
α-$ThNi_2P_2$					
Th	4c	0.26129(3)	1/4	0.33017(2)	0.392(4)
Ni1	4c	0.4490(2)	1/4	0.6236(1)	0.72(2)
Ni2	4c	0.4188(1)	1/4	0.0488(1)	0.51(2)
P1	4c	0.0299(3)	1/4	0.6613(2)	0.54(3)
P2	4c	0.1436(3)	1/4	0.0478(2)	0.49(3)

Atom	P4/nmm	x	y	z	B_{eq}
β-$ThNi_2P_2$					
Th	2c	1/4	1/4	0.2486(1)	0.233(4)
Ni1	2a	1/4	3/4	0	0.56(2)
Ni2	2c	1/4	1/4	0.6141(3)	0.63(3)
P1	2b	1/4	3/4	1/2	0.77(5)
P2	2c	1/4	1/4	0.8709(6)	0.26(4)

Table III. Interatomic distances [pm] in the structures of α- and β-$ThNi_2P_2$. All distances shorter than 490 pm (Th–Th, Th–Ni), 340 pm (Th–P, Ni–Ni, Ni–P), and 320 pm (P–P) are listed. Standard deviations computed from those of the positional parameters and the lattice constants are given in parentheses.

α-$ThNi_2P_2$

Th:	1	P2	293.5(3)	Ni1:	1	P1	221.3(4)	P1:	1	Ni1	221.3(4)
	2	P2	301.0(3)		2	P2	223.9(2)		1	Ni2	225.5(4)
	2	P1	309.3(3)		1	P2	231.8(4)		2	Ni2	229.8(2)
	2	P1	309.7(3)		2	Ni1	323.6(2)		2	Th	309.3(3)
	1	P2	335.5(3)		2	Th	312.0(2)		2	Th	309.7(3)
	2	Ni2	304.8(2)		1	Th	326.5(2)	P2:	2	Ni1	223.9(2)
	2	Ni1	312.0(2)		2	Th	331.2(2)		1	Ni2	225.6(4)
	1	Ni1	326.5(2)	Ni2:	1	P1	225.5(4)		1	Ni1	231.8(4)
	2	Ni2	326.7(2)		1	P2	225.6(4)		1	Th	293.5(3)
	2	Ni1	331.2(2)		2	P1	229.8(2)		2	Th	301.0(3)
	2	Th	394.3(1)		2	Ni2	256.5(2)		1	Th	335.5(3)
	2	Th	439.0(1)		2	Th	304.8(2)				
					2	Th	326.7(2)				

β-$ThNi_2P_2$

Th:	4	P1	306.3(2)	Ni1:	4	P2	235.5(3)	P1:	4	Ni2	229.0(2)
	4	P2	308.5(3)		4	Ni1	288.9(1)		4	P1	288.9(1)
	4	Ni1	304.4(2)		4	Th	304.4(2)		4	Th	306.3(2)
	4	Ni2	314.6(2)	Ni2:	4	P1	229.0(2)	P2:	1	Ni2	233.2(7)
	1	Ni2	331.9(4)		1	P2	233.2(7)		4	Ni1	235.5(3)
	4	Th	408.5(1)		4	Th	314.6(2)		4	Th	308.5(3)
					1	Th	331.9(4)				

to the standardized setting [16] of the isopointal structure $ThRu_2P_2$ [6]. For the calculation of the interatomic distances (Table III) the lattice constants obtained from the powder data were used, because the lattice constants calculated from the single-crystal diffractometer data are affected by systematic errors due to absorption effects. Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper. Listings of the anisotropic thermal parameters and the structure factors are available*.

Discussion

First we will discuss the similarities and differences of the two modifications of $ThNi_2P_2$ and then consider the differences between the closely related, almost isotypic structures of $ThRu_2P_2$ and α-$ThNi_2P_2$. The refinement of the occupancy parameters showed that both modifications of $ThNi_2P_2$ are at least very close to the ideal composition. Nevertheless, small homogeneity ranges can be expected for both modifications, and these will affect the temperatures at which the two modifications are in equilibrium with each other. This may explain the fact, that we were not successful in preparing the β-modification in pure form at 1000 °C. At this temperature always varying amounts of the α-modification were present in the samples, whereas at lower temperatures only the α-modification was obtained. It should be possible to prepare the β-modification in pure form at higher temperatures, however, at higher annealing temperatures the samples tend to react with the silica tubes and arc-melting leads to phosphorus losses. The fact that the high-temperature modification transforms completely to the low-temperature modification by annealing at lower temperatures (800 °C) suggsts that the high-temperature modification is not stabilized by impurities.

The structures of the two modifications (Fig. 1) are related, however, they are not that similar, that they could transform into each other by a displacive phase transition. In both modifications the thorium atoms have eight phosphorus neighbors in a more or less distorted square antiprismatic arrangement, at average distances of 308.6 (α) and 307.4 pm (β), and nine nickel neighbors with average distances of 319.5 and 312.0 pm, respectively. Certainly the Th–Ni interactions will contribute less to the stability of the structures, but at least those interactions with the shorter distances of around 305 pm (which are similar to the sum of the atomic radii of 304 pm [17, 18]) should not be discounted entirely.

Most nickel atoms are tetrahedrally coordinated by phosphorus atoms; the Ni1 and Ni2 atoms of the α-modification at average distances of 225.2 and 227.7 pm, respectively. The latter distance is somewhat greater, because the Ni2 atoms form two additional Ni–Ni bonds with a bond distance of 256.5 pm. The Ni1 atom of the β-modification is also tetrahedrally coordinated by phosphorus atoms, however, the bond distance of 235.5 pm is surprisingly large. To some extent this may be rationalized by the additional four nickel and four thorium neighbors at 288.9 and 304.4 pm, respectively. However, this relatively large Ni1–P2 distance of 235.5 pm is better understood from the coordination of the P2 atom, which is the only one

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* They may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the registry no CSD 58287, the names of the authors, and the journal citation.

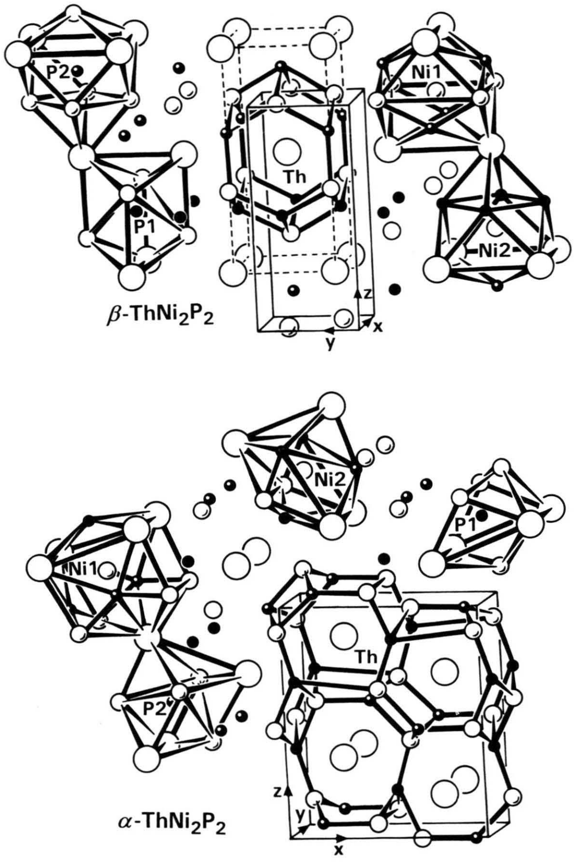

Fig. 1. Crystal structures and coordination polyhedra of the high-temperature (β) and low-temperature (α) modifications of ThNi$_2$P$_2$. The tetragonal cell of the β-modification, drawn with continuous lines, corresponds to the setting of Table II.

with five nickel neighbors, while the three other phosphorus atoms of the two compounds have only four nickel neighbors. A similar situation was found for CeRh$_2$P$_2$, which also crystallizes with CaBe$_2$Ge$_2$ type structure [19], where the Rh–P distance of the tetrahedrally coordinated rhodium atom is again greater (246.1 pm) than the average Rh–P distance of the square-pyramidal one (234.0 pm). Finally, the Ni2 atom of the β-modification has five phosphorus neighbors at an average distance of 229.8 pm, and this distance is greater than the average Ni–P distances of the tetrahedrally coordinated nickel atoms of the α-modification, as it should be.

All phosphorus atoms of both modifications have four thorium neighbors at comparable average distances. In addition, most of them have four nickel neighbors with more (P1 of the α-modification) or less distorted tetrahedral coordination. The average P–Ni distances are similar with 226.6, 226.3, and 229.0 pm for the P1 and P2 atoms of the α- and the P1 atom of the β-modification, respectively. The P2 atom of the β-modification has five nickel neighbors in square pyramidal arrangement at an average distance of 235.0 pm.

In Fig. 2 we accentuate some similarities and differences of the two structures. In the upper part of that figure the short interatomic distances within the polyanionic nickel-phosphorus networks are emphasized. In the lower part the linkages of the distorted trigonal metal prisms around the P1 and P2 atoms of the α- and the β-modification, respectively, are shown (the other phosphorus atoms have other arrangements of their metal neighbors). The trigonal prismatic coordination (augmented by three additional neighbors outside the rectangular faces of the prisms) represents the usual phosphorus coordination in phosphides with a higher metal content, and the various ways by which the trigonal prisms are linked with each other are frequently used to visualize the similarities and differences of such structures [20–24 and references therein]. It can be seen that both, the more or less covalently bonded nickel-phosphorus network and the linking of the trigonal metal prisms discussed above, are sufficiently different in the two structures to rule out a displacive phase transition.

There are some empirical rules, which distinguish the high (β) and low (α) temperature forms of two modifications for a given composition. Usually the high temperature form has a higher symmetry, a smaller cell content, and a smaller number of variable positional parameters. This is also the case for the two modifications of ThNi$_2$P$_2$. The high temperature modification has higher symmetry: P4/nmm with a 16-fold *vs.* Pnma with an 8-fold general position; it has a smaller cell content: $Z = 2$ *vs.* $Z = 4$; and it has the smaller number of variable positional parameters: three in the high temperature β-form *vs.* ten in the low temperature α-form. Frequently the high temperature form also has the lower density, but there are well known exceptions, like the two modifications of tin, where the higher entropy of the conduction electrons contributes to the stability of the metallic

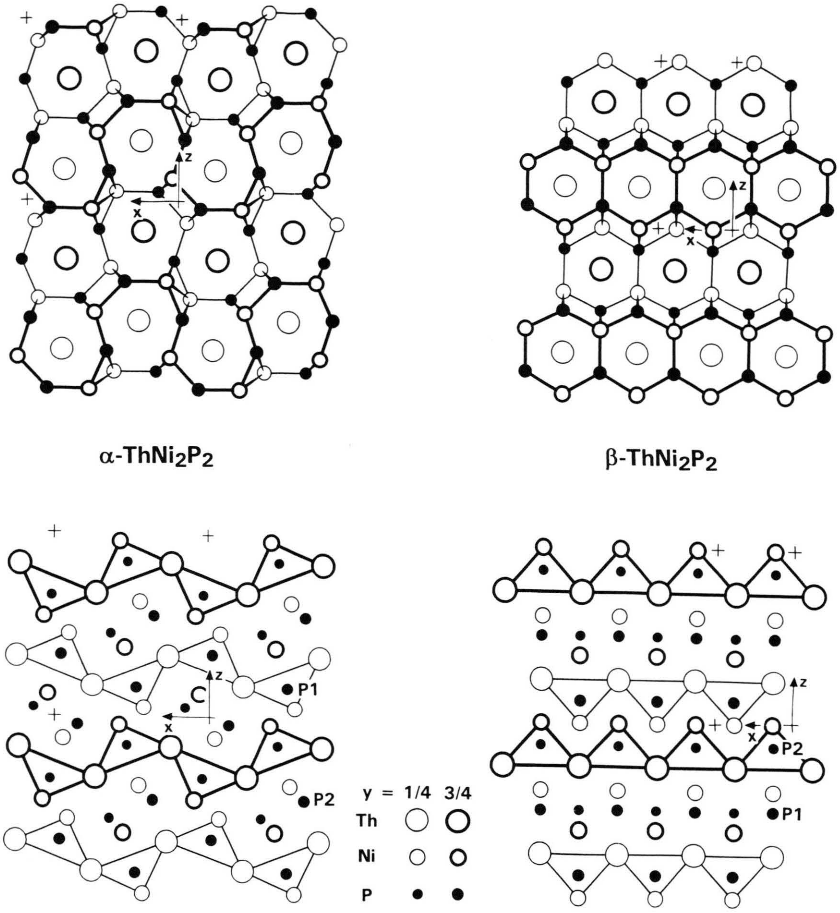

Fig. 2. Structural differences of α- and β-$ThNi_2P_2$. The upper part of the figure shows the nickel-phosphorus networks. Atoms connected by thin and thick lines are separated by half a translation period of the projection direction. In both structures one half of the phosphorus atoms has (augmented) trigonal prismatic metal coordination. The linkages of these trigonal prisms are emphasized in the lower part of the figure.

high temperature modification. One may speculate, whether the two modifications of $ThNi_2P_2$ also represent such an exception. In any case, the high temperature form has a higher density ($9.02\ g \cdot cm^{-3}$) than the low temperature form ($8.62\ g \cdot cm^{-3}$). The high temperature form also has one nickel (Ni2) and one phosphorus atom (P2) with higher Ni–P coordination than the other nickel and phosphorus atoms of the two modifications. A fourfold coordination of the phosphorus atoms is frequently observed for phosphorus compounds, which can be rationalized by localized two-electron bonds. The fivefold nickel coordination of the P2 atom in the β-modification suggests a greater degree of electron delocalization. Both modifications are possibly metallic conductors, however, the high temperature form with the somewhat higher coordination number for some atoms may have a higher density of states at the Fermi level.

The structures of the three compounds $ThRu_2P_2$, α-$ThNi_2P_2$, and $BaCu_2S_2$ might be considered as isotypic, although their near-neighbor coordinations are different. Parthé and Gelato [25] have proposed to call such a relationship isopointal. Fig. 3 shows that the structure of α-$ThNi_2P_2$ is intermediate between those of $ThRu_2P_2$ and $BaCu_2S_2$. This is also evident from the *c/a* ratios of the three compounds, which vary from 1.39 for $ThRu_2P_2$ *via* 1.20 for α-$ThNi_2P_2$ to 1.12 for $BaCu_2S_2$.

$ThRu_2P_2$ and α-$ThNi_2P_2$ differ only by their transition metal component. The radius for the coordination number 12 of ruthenium (133.9 pm [17, 18]) is 1.075 times greater than that of nickel (124.6 pm), but the lattice constant *a* of the ruthenium compound (753.15 pm) is 0.9188 times smaller than that of the nickel compound (819.69 pm). The two compounds might form a continuous series of solid solution, however, not

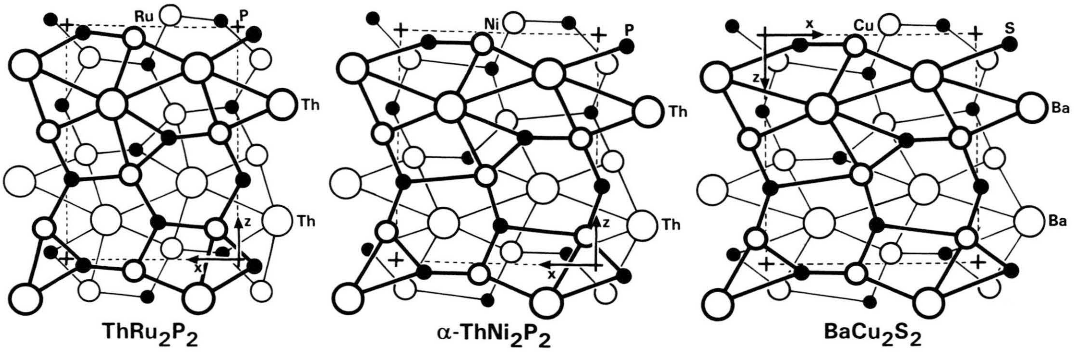

Fig. 3. The relationship of the three isopointal structures of $ThRu_2P_2$, α-$ThNi_2P_2$, and $BaCu_2S_2$. Atoms at the same heights of the projection direction are connected by thick (y = 3/4) and thin (y = 1/4) lines. Most of these lines represent short interatomic distances in the structure of $ThRu_2P_2$. This is not always the case in the structure of $BaCu_2S_2$. The structure of α-$ThNi_2P_2$ is in between these two extremes.

necessarily with a continuous change of the lattice constant a. It seems possible that intermediate compositions might change discontinuously with temperature by a displacive phase transition from one axial ratio c/a to the other, similar to the phase transitions proposed for $ThCr_2Si_2$ type compounds with differing c/a ratio [26] and verified for the composition $Ca_{0.60}Sr_{0.40}Co_2P_2$ [27].

The near neighbor coordinations of the ruthenium atoms in $ThRu_2P_2$ and of the nickel atoms in α-$ThNi_2P_2$ are different. In general, the ruthenium atoms have the higher coordination numbers: the Ru 1 atom has five phosphorus neighbors (*vs.* four for Ni 1) and there are more Ru–Ru interactions in $ThRu_2P_2$ [6] than there are Ni–Ni interactions in α-$ThNi_2P_2$. This is probably not only a trivial consequence of the larger size of the ruthenium atom, it very likely also has to do with the higher electron count of the nickel atoms. In this part of the Periodic Table a higher electron count leads to weaker bonding interactions as is obvious from the dramatic decrease of the melting temperatures in going from tungsten to mercury.

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