

The Crystal Structures of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ and ThFe_5P_3

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The new compounds $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ and ThFe_5P_3 were prepared in well-crystallized form using a tin flux. Their crystal structures were determined from single-crystal X ray data. $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ ($x = 0.36(3)$) is monoclinic: $C2/m$, $a = 2464.8(6)$ pm, $b = 377.3(1)$ pm, $c = 930.3(2)$ pm, $\beta = 91.25(3)^\circ$, $Z = 2$, $R = 0.024$. ThFe_5P_3 has a YCo_5P_3 -type structure: $Pnma$, $a = 1210.8(2)$ pm, $b = 376.7(1)$ pm, $c = 1058.1(4)$ pm, $Z = 4$, $R = 0.024$. The compounds belong to a large family of structures with a metal: nonmetal ratio of exactly or nearly 2:1. In these structures all phosphorus atoms are surrounded by six metal atoms forming a trigonal prism with three additional metal atoms capping the rectangular faces of the prism. The iron atoms in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ and ThFe_5P_3 have tetrahedral and square-pyramidal phosphorus coordination. One iron atom of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ is situated in a rectangle of phosphorus atoms. Both compounds have numerous iron-iron bonds with distances as short as 238 pm. The oxygen atoms of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ are octahedrally coordinated by four thorium and two iron atoms. © 1995 Academic Press, Inc.

INTRODUCTION

Only few ternary phosphides containing thorium as the most electropositive component are known: $\text{Th}_6\text{Co}_{20}\text{P}_{13}$ (1) with $\text{Zr}_6\text{Ni}_{20}\text{P}_{13}$ -type structure, ThCu_2P_2 (2) (Ce_2SO_2 -type), ThCo_2P_2 (3) (CaBe_2Ge_2 -type), ThRu_2P_2 (4) (BaCu_2S_2 -type), $\text{Th}_5\text{Ru}_{19}\text{P}_{12}$ (5) ($\text{Sc}_5\text{Co}_{19}\text{P}_{12}$ -type), ThFe_4P_2 (6) (SmNi_4P_2 -type), and $\text{Th}_5\text{Fe}_{19}\text{P}_{12}$ (6) (own structure type). Here we report about ThFe_5P_3 and $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$. The latter compound might be considered as an interstitial oxide, a suboxide, or a phosphide oxide. Not many phosphide oxides are known. The compounds $\text{Na}_3\text{M}_7(\text{P}_3)_3\text{O}$ ($M = \text{Sr}, \text{Eu}$) (7) and $\text{M}_4\text{P}_2\text{O}$ ($M = \text{Sr}, \text{Ba}$) (8) were reported recently.

SAMPLE PREPARATION AND LATTICE CONSTANTS

Starting materials were ingots of thorium (nominal purity 99.9%), iron powder (Merck, >99.9%), small pieces of red phosphorus (Hoechst-Knapsack, "ultrapure"), and granules of tin (Merck, 99.9%). Filings of thorium were prepared in dried paraffin oil, which subsequently was removed by washing with dried hexane in an argon

atmosphere. The filings were stored under vacuum and they were not allowed to come in contact with air prior to the reactions. The compounds were originally prepared with the tin flux technique. The mixed components were sealed in evacuated silica tubes, placed vertically in a furnace, and heated slowly ($20^\circ\text{C}/\text{hr}$) to the reaction temperature of 960°C . After annealing for 21 days the ampoules were cooled ($20^\circ\text{C}/\text{hr}$) to room temperature. The tin-rich matrix was dissolved in hot, slightly diluted (1:1) hydrochloric acid.

ThFe_5P_3 was obtained as the major product in samples with the starting ratios $\text{Th}:\text{Fe}:\text{P}:\text{Sn}$ varying among 6:10.5:8.5:75, 3.8:15:6.2:75, and 2.5:18.8:3.7:75. Crystals of this compound are shiny, black, and needle-shaped. The crystals of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ are also needle-shaped, however, with a golden or brownish tint, depending on the surface roughness. The compound $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ was observed first in several samples as a byproduct. In the sample with the starting ratio $\text{Th}:\text{Fe}:\text{P}:\text{Sn} = 4:16:8:72$ it occurred together with ThFe_5P_3 and ThFe_2P_2 (9). This compound cannot be prepared when the same starting components are reacted in alumina containers. Apparently the oxygen content is due to the silica of the tubes, which is reduced by thorium. Accordingly the crystals of the other byproduct ThFe_2P_2 contain 4 at% silicon. The oxygen content of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ was first detected in the course of the structure determination. To exclude the possibility of the interstitial atoms being nitrogen or carbon we investigated freshly broken surfaces of these crystals in a scanning electron microscope with energy dispersive X ray analyses. The oxygen content of these surfaces was rather high, apparently due to the freshly formed surface oxides by reaction with air; however, the careful analysis did not reveal any carbon or nitrogen.

Subsequently both compounds were prepared without the tin flux using alumina containers, which in turn were sealed in evacuated silica tubes. Starting materials were powders of the elemental components with the ideal composition and oxygen was introduced in the form of FeO . The samples were reacted for 1 week at 650°C , ground to powders, compacted to pellets, and annealed again for 3

weeks at 1000°C. While ThFe_5P_3 was single phase, the sample of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ contained some ThFe_5P_3 as an impurity. We were not successful in preparing the corresponding $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ -type compounds by adding boron, carbon, or nitrogen (in form of Fe_4N) in the place of oxygen.

All samples were characterized through their Guinier powder patterns with $\text{CuK}\alpha_1$ radiation using α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as internal standard. The lattice constants were obtained by least-squares fits. To assure proper indexing the intensities of the diffraction lines were compared with the calculated ones.

STRUCTURE DETERMINATIONS

Single crystals of the two compounds were examined using Weissenberg cameras. The crystal of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ showed monoclinic symmetry with systematic extinctions compatible with the space groups $C2$, Cm , and $C2/m$, of which the centrosymmetric group $C2/m$ was found to be correct during the structure determination. ThFe_5P_3 was recognized to be isotypic with YCo_5P_3 (10). Intensity data of single crystals from both compounds were collected on an automated Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation, a scintillation counter with pulse-height

discriminator and background counts at both ends of each $\theta/2\theta$ scan. The crystallographic data are listed in Table 1.

The structure of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ was determined by direct methods (11), which resulted in the positions of the thorium and some iron atoms. The other atoms were located by difference Fourier syntheses. The structures were refined by full-matrix least-squares cycles with atomic scattering factors (12), corrected for anomalous dispersion (13). Parameters accounting for isotropic secondary extinction were optimized and the weights were assigned according to the counting statistics. All metal atoms were refined with anisotropic thermal parameters, the phosphorus atoms with isotropic ones. The residual for the structure of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ before adding the oxygen atom was $R = 0.028$. At this stage the difference Fourier synthesis contained a relatively high peak of $12.7 e/\text{\AA}^3$ at the position $0, 1/2, 1/2$. After adding an oxygen atom at this site a residual of $R = 0.025$ was obtained. The variation of the occupancy parameters (with fixed scale factor) showed that all atomic positions were fully occupied (occupancy parameters varied between $96 \pm 1\%$ for the P2 atoms and $100.3 \pm 0.1\%$ for both Th atoms) with the exception of the oxygen position, which yielded an occupancy value of $64 \pm 3\%$. Thus, in the final least-squares cycles all occupancy parameters were fixed at

TABLE 1
Crystal Data for $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ and ThFe_5P_3 ^a

Compound	$\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$	ThFe_5P_3
Structure type	$\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$	YCo_5P_3
Space group	$C2/m$ (No. 12)	$Pnma$ (No. 62)
Lattice constants from Guinier powder data		
a (pm)	2464.8(6)	1210.8(2)
b (pm)	377.3(1)	376.7(1)
c (pm)	930.3(2)	1058.1(4)
β (°)	91.25(3)	
V (nm ³)	0.8650(4)	0.4826(2)
Formula units/cell, Z	2	4
Formula weight	2203.3	604.2
Calculated density (g/cm ³)	8.46	8.32
Crystal dimensions (μm)	$20 \times 20 \times 100$	$10 \times 10 \times 130$
$\theta/2\theta$ scans up to	$2\theta = 65^\circ$	$2\theta = 75^\circ$
Range in h, k, l	$\pm 37, +5, \pm 14$	$\pm 20, \pm 18, +7$
Total number of reflections	3574	5690
Absorption corrections from psi scans with the ratio of the highest to the lowest transmission	1.30	1.12
Unique reflections	1830	1524
Inner residual	$R_i = 0.022$	$R_i = 0.042$
Reflections with $I > 3\sigma(I)$	1199	809
Number of variables	83	47
Conventional residual	$R = 0.024$	$R = 0.024$
Weighted residual	$R_w = 0.024$	$R_w = 0.023$

^a Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

their ideal values with the exception of that for the oxygen atom. A final difference Fourier synthesis showed no peaks higher than $2.2 e/\text{\AA}^3$. The exact formula for the crystal used for the structure determination is $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ with $x = 0.36(3)$; however, since that crystal had been prepared under conditions with low oxygen partial pressure, it seems likely that the ideal occupancy of the oxygen position could be obtained if enough oxygen were available during the formation of the crystals. For that reason and for simplicity we sometimes also use the ideal formula $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ for this compound.

The refinement of the structure of ThFe_5P_3 went smoothly; occupancy parameters varied between $97.5 \pm 0.4\%$ for Fe1 and $100.3 \pm 0.1\%$ for Th1, and the ideal occupancy parameters were assumed during the final cycles. The final atomic parameters and interatomic dis-

tances are given in Tables 2–4. A projection of the structure of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ is shown in Fig. 1. Listings of the anisotropic thermal parameters and the structure factors are available from the authors.

DISCUSSION

The compounds $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ and ThFe_5P_3 belong to a large family of structures of borides and silicides (15) as well as phosphides (6, 16–22) and their homologues with a metal to metalloid ratio of exactly or close to 2:1. In these compounds the metalloid atoms (B, Si, P) are situated in trigonal prisms, which are usually capped by three additional metal atoms outside the rectangular faces of the prisms. These structures are frequently categorized by the way these trigonal prisms are linked to each other. In ThFe_5P_3 (Fig. 2) the trigonal prisms form "windmills," which are linked by common edges, thus forming infinite chains in the horizontal direction. Since these prisms also share the trigonal faces in the third dimension (the viewing direction) the whole structure may be considered as being built up by two-dimensional infinite sheets of such trigonal prisms.

In the structure of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ (when viewed along the short translation period) the trigonal prisms around the phosphorus atoms form 10-membered chains with windmills at both ends. Therefore these building elements are only one-dimensionally infinite, with the projection direction as the infinite dimension. The oxygen atoms terminate the chains. They thus have a real function in the structure and it is not surprising that the compound cannot be formed in the absence of oxygen. In that sense the oxygen in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ is as essential as in the sulfide oxides $\text{Ln}_{10}\text{S}_{14}\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$) (23, 24). The role of small amounts of impurities, which are necessary to stabilize a structure is well known for the structure of β -tungsten (W_3O) and the Nowotny phases, e.g., $\text{Mo}_5\text{Si}_3\text{C}_{1-x}$ (25). In that silicide carbide the carbon atoms are octahedrally coordinated by molybdenum atoms, as is frequently the case for carbides of the early transition elements. The oxygen atoms in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ are also octahedrally coordinated by metal atoms with four thorium atoms and two iron atoms in *trans* position. This coordination is comparable to the octahedra $\text{Th}_4\text{Fe}_2\text{C}$, $\text{U}_4\text{Mo}_2\text{C}$, and $\text{U}_4\text{Re}_2\text{C}$ in ThFe_2SiC (26), UMoC_2 (27), and $\text{U}_3\text{Re}_3\text{C}_8$ (28). Interstitial carbides and oxides have similar interatomic distances as can be seen by comparing the lattice constants of UC with $a = 496.2$ pm (29) and UO with $a = 492$ pm (30), both with NaCl-type structure. Thus, the interatomic distances of the interstitial oxygen atom in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ of O–Fe with 183.5(3) pm (2x) and O–Th with 267.4(1) pm (4x) compare well with the distances of the carbon atom in ThFe_2SiC of C–Fe with 184.2(1) pm (2x) and C–Th with 266.0(1) pm (4x).

TABLE 2
Atomic Parameters of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ and $\text{ThFe}_5\text{P}_3^a$

	x	y	z	B
$\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$				
Th1	0.04469(2)	0	0.66837(4)	0.300(6)
Th2	0.66450(2)	0	0.16963(4)	0.280(6)
Fe1	0.09668(7)	0	0.0002(2)	0.52(3)
Fe2	0.14225(7)	0	0.4350(2)	0.47(3)
Fe3	0.19949(7)	0	0.6846(2)	0.63(3)
Fe4	0.25954(7)	0	0.1047(2)	0.56(3)
Fe5	0.28475(6)	0	0.5266(2)	0.43(3)
Fe6	0.36101(7)	0	0.1777(2)	0.55(3)
Fe7	0.53613(7)	0	0.1476(2)	0.54(3)
Fe8	0.56488(7)	0	0.4069(3)	0.51(3)
Fe9	0	0	0	0.65(4)
P1	0.0764(1)	0	0.2542(3)	0.48(4)
P2	0.2297(1)	0	0.3377(3)	0.52(4)
P3	0.3649(1)	0	0.4215(3)	0.61(4)
P4	0.4432(1)	0	0.0881(3)	0.53(4)
P5	0.8131(1)	0	0.0702(3)	0.49(4)
O	0	1/2	1/2	0.4(2)
ThFe_5P_3				
Th1	0.20409(3)	1/4	0.91835(3)	0.298(4)
Fe1	0.4881(1)	1/4	0.7956(1)	0.62(2)
Fe2	0.9901(1)	1/4	0.0959(2)	0.59(2)
Fe3	0.6751(1)	1/4	0.2791(1)	0.53(2)
Fe4	0.1979(1)	1/4	0.6209(1)	0.49(2)
Fe5	0.4339(1)	1/4	0.0337(1)	0.39(2)
P1	0.6109(2)	1/4	0.0784(3)	0.61(3)
P2	0.3689(2)	1/4	0.2278(3)	0.59(3)
P3	0.8940(2)	1/4	0.8950(3)	0.66(4)

^a For $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ the positional parameters are given in the standardized form proposed by Gelato and Parthé (14), those of ThFe_5P_3 corresponding to the setting of YCo_5P_3 (10). The last column contains the isotropic thermal parameters of the phosphorus atoms and the equivalent isotropic B values of the anisotropic temperature parameters of the metal atoms ($\times 100$, in units of nm^2). The occupancy of the oxygen position in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ was found to be $64 \pm 3\%$, i.e., $x = 0.36(3)$.

TABLE 3
Interatomic Distances in the Structure of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$ ^a

Th1:	2O	267.4(1)	Fe2:	1P1	231.2(4)	Fe6:	1P4	220.8(4)	P1:	2Th2	299.5(3)
	2P4	295.8(3)		2P3	232.0(3)		1P3	226.8(5)		1Th1	308.6(3)
	2P3	305.1(3)		1P2	235.5(3)		2P5	242.9(3)		1Fe2	231.2(4)
	1P1	308.6(4)		2Fe5	262.6(2)		1Fe4	257.7(3)		2Fe7	234.2(3)
	2Fe8	312.7(2)		2Fe8	269.1(3)		2Fe1	273.1(3)		2Fe8	238.3(3)
	2Fe7	325.7(2)		1Fe3	269.1(3)		2Fe3	274.0(3)	P2:	1Fe1	242.6(4)
	1Fe2	327.5(3)		2Th2	316.4(2)		1Th2	327.8(2)		2Th2	291.1(3)
	2Fe6	329.7(2)		1Th1	327.5(3)		2Th1	329.7(2)		1Fe5	219.7(4)
	1Fe9	329.9(1)	Fe3:	1P5	230.8(4)	Fe7:	1P4	226.1(4)		2Fe5	230.2(3)
	1Fe1	331.7(3)		2P2	258.2(3)		2P1	234.2(3)		1Fe4	230.5(4)
	2Fe8	335.6(2)		2P3	264.3(3)		1P4	234.4(3)		1Fe2	235.5(3)
	2Th1	377.3(1)		1Fe5	259.1(3)		2Fe9	248.7(2)		2Fe3	258.2(3)
	1Th1	379.0(2)		1Fe2	269.1(3)		1Fe8	250.0(3)	P3:	2Th1	305.1(3)
	1Fe3	381.5(3)		2Fe6	274.0(3)		2Fe1	278.5(3)		1Fe5	222.3(4)
Th2:	2P2	291.1(3)		2Fe5	275.8(3)		1Fe7	324.0(3)		1Fe6	226.8(5)
	2P5	298.3(3)		2Fe4	288.7(3)		1Th2	316.6(3)		2Fe2	232.0(3)
	2P1	299.5(3)		1Th2	358.9(3)		2Th1	325.7(2)		1Fe8	232.9(4)
	2Fe1	295.3(2)	Fe4:	1Th1	381.5(3)	Fe8:	1O	183.5(3)		2Fe3	264.3(3)
	1Fe5	306.5(3)		1P2	230.5(4)		1P3	232.9(4)	P4:	2Th1	295.8(3)
	2Fe4	307.8(2)		2P5	232.9(3)		2P1	238.3(3)		1Fe6	220.8(4)
	2Fe2	316.4(3)		1P5	239.3(4)		1Fe7	250.0(3)		1Fe7	226.1(4)
	1Fe7	316.6(2)		1Fe6	257.7(3)		2Fe2	269.1(3)		2Fe1	227.3(3)
	1Fe4	319.8(3)		2Fe4	274.5(3)		2Th1	312.7(2)		1Fe7	234.4(4)
	1Fe6	327.8(3)		2Fe3	288.7(3)		1Th2	333.8(3)		2Fe9	249.8(3)
	1Fe8	333.8(3)		2Th2	307.8(2)		2Th1	335.6(2)	P5:	2Th2	298.3(3)
	1Fe3	358.9(3)		1Th2	319.8(3)	Fe9:	4P4	249.8(3)		1Fe3	230.8(4)
	2Th2	377.3(1)	Fe5:	1P2	219.7(4)		2Fe1	238.3(2)		2Fe4	232.9(3)
Fe1:	2P4	227.3(3)		1P3	222.3(4)		4Fe7	248.7(2)		1Fe1	233.2(4)
	1P5	233.2(4)		2P2	230.2(3)		2Th1	329.9(1)		1Fe4	239.3(3)
	1P1	242.6(4)		2Fe5	258.9(2)					2Fe6	242.9(3)
	1Fe9	238.3(2)		1Fe3	259.1(3)				O:	4Th1	267.4(1)
	2Fe6	273.1(3)		2Fe2	262.6(2)					2Fe8	183.5(3)
	2Fe7	278.5(3)		2Fe3	275.8(3)						
	2Th2	295.3(2)		1Th2	306.5(3)						
	1Th1	331.7(3)									

^a All distances shorter than 550 pm (Th–Th), 390 pm (Th–Fe, Th–P), 350 pm (Fe–Fe, P–P), and 295 pm (Fe–P) are listed. The oxygen atoms have no further neighbors up to 335 pm. Standard deviations computed from those of the positional parameters and the lattice constants are given in parentheses.

The coordination polyhedra of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ and ThFe_5P_3 are similar. Since the YCo_5P_3 -type structure has been discussed before (10), we will focus our attention on the structure of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$. Both thorium atoms of that structure have high coordination numbers with a large number of metal–metal interactions. Those with the larger interatomic distances are certainly contributing little to the stability of the compound. Table 3 includes all distances, which correspond to the coordination polyhedra shown in Fig. 1. The bonds formed by the oxygen and phosphorus atoms are more important. This is reflected by the average Th–P distances of 302 pm for Th1 (with two O and five P neighbors) and 296 pm for Th2 (six P neighbors).

The coordination polyhedra of the iron atoms are simi-

lar to those of the transition elements in other members of this large family of structures. The Fe1, Fe2, Fe4, Fe5, Fe6, and Fe7 atoms have tetrahedral phosphorus coordinations (plus eight additional metal neighbors) with average Fe–P distances ranging between 232.2 and 233.9 pm with the exception of the Fe5 atom, where the average Fe–P distance is 225.6 pm. This considerably smaller average Fe–P distance correlates with the fact that this iron atom has only one thorium neighbor, while the other tetrahedral iron atoms have three. It was argued before (6) that the higher number of thorium neighbors (which is compensated by a smaller number of iron neighbors) in the coordination shell of the iron atoms contributes more electrons to Fe–P antibonding states and therefore leads to longer average Fe–P distances. The Fe3 atom has five

TABLE 4
Interatomic Distances in the Structure of $\text{ThFe}_3\text{P}_3^a$

Th:	2P2	289.7(3)	Fe2:	2P3	235.1(2)	Fe4:	2P2	234.1(2)	P1:	2Th	292.7(2)
	2P1	292.7(2)		1P2	237.3(3)		1P1	235.7(4)		1Fe5	219.5(3)
	2P3	297.6(2)		1P3	242.4(3)		1P3	238.0(4)		1Fe3	226.1(3)
	2Fe2	301.7(2)		1Fe3	260.0(2)		2Fe5	263.5(2)		2Fe5	229.1(2)
	1Fe5	303.8(2)		2Fe2	278.0(2)		2Fe3	265.2(2)		1Fe4	235.7(4)
	2Fe4	309.0(2)		2Fe1	284.3(2)		1Fe1	269.0(3)		2Fe1	260.0(3)
	1Fe4	314.8(2)		2Th	301.7(2)		2Th	309.0(2)	P2:	2Th	289.7(2)
	2Fe3	317.1(2)		1Th	320.0(2)		1Th	314.8(2)		1Fe5	219.9(3)
	1Fe2	320.0(2)	Fe3:	1P1	226.1(3)	Fe5:	1P1	219.5(3)		2Fe4	234.1(2)
	1Fe3	322.1(2)		1P2	234.9(3)		1P2	219.9(3)		1Fe3	234.9(3)
	1Fe1	345.9(2)		2P3	239.9(2)		2P1	229.1(2)		1Fe2	237.3(3)
	1Fe1	367.6(2)		1Fe2	260.0(2)		2Fe5	257.3(2)		2Fe1	257.0(2)
	2Th	376.7(1)		2Fe4	265.2(2)		1Fe1	260.3(2)	P3:	2Th	297.6(2)
Fe1:	1P3	231.7(3)		2Fe1	284.2(2)		2Fe4	263.5(2)		1Fe1	231.7(3)
	2P2	257.0(3)		2Th	317.1(2)		2Fe1	277.5(2)		2Fe2	235.1(2)
	2P1	260.0(3)		1Th	322.1(2)		1Th	303.8(2)		1Fe4	238.0(4)
	1Fe5	260.3(2)								2Fe3	239.9(2)
	1Fe4	269.0(3)								1Fe2	242.4(3)
	2Fe5	277.5(2)									
	2Fe3	284.2(2)									
	2Fe2	284.3(2)									
	1Th	345.9(2)									
	1Th	367.6(2)									

^a All distances shorter than 550 pm (Th–Th), 370 pm (Th–Fe, Th–P), 330 pm (Fe–Fe, P–P), and 310 pm (Fe–P) are listed.

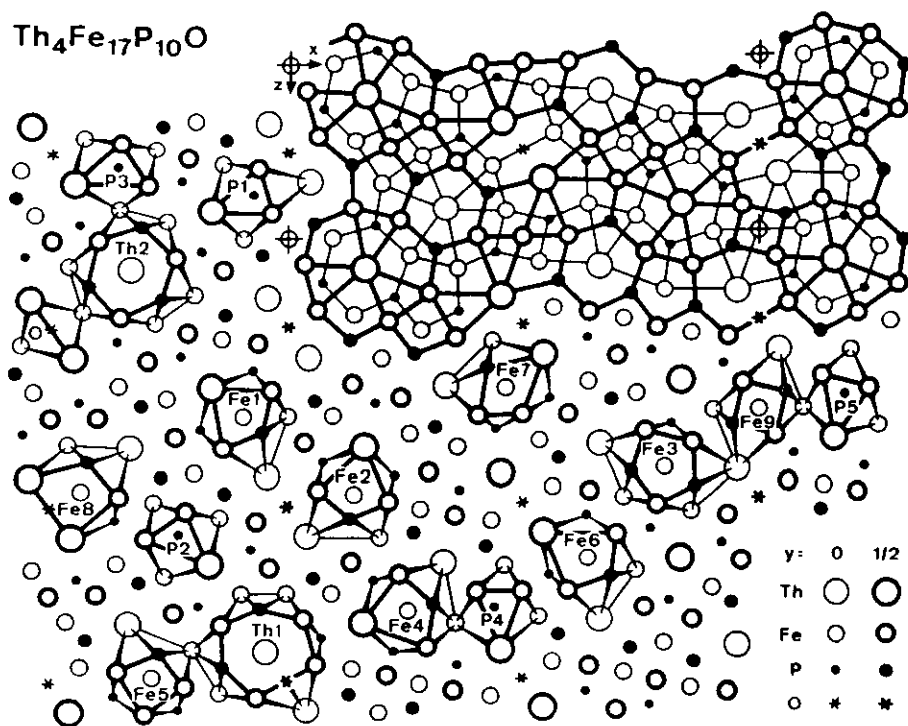


FIG. 1. Crystal structure and coordination polyhedra of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$. All atoms are situated on mirror planes at $y = 0$ and $1/2$. Atoms at these heights are connected by thin and thick lines, respectively, in the upper right-hand part of the drawing.

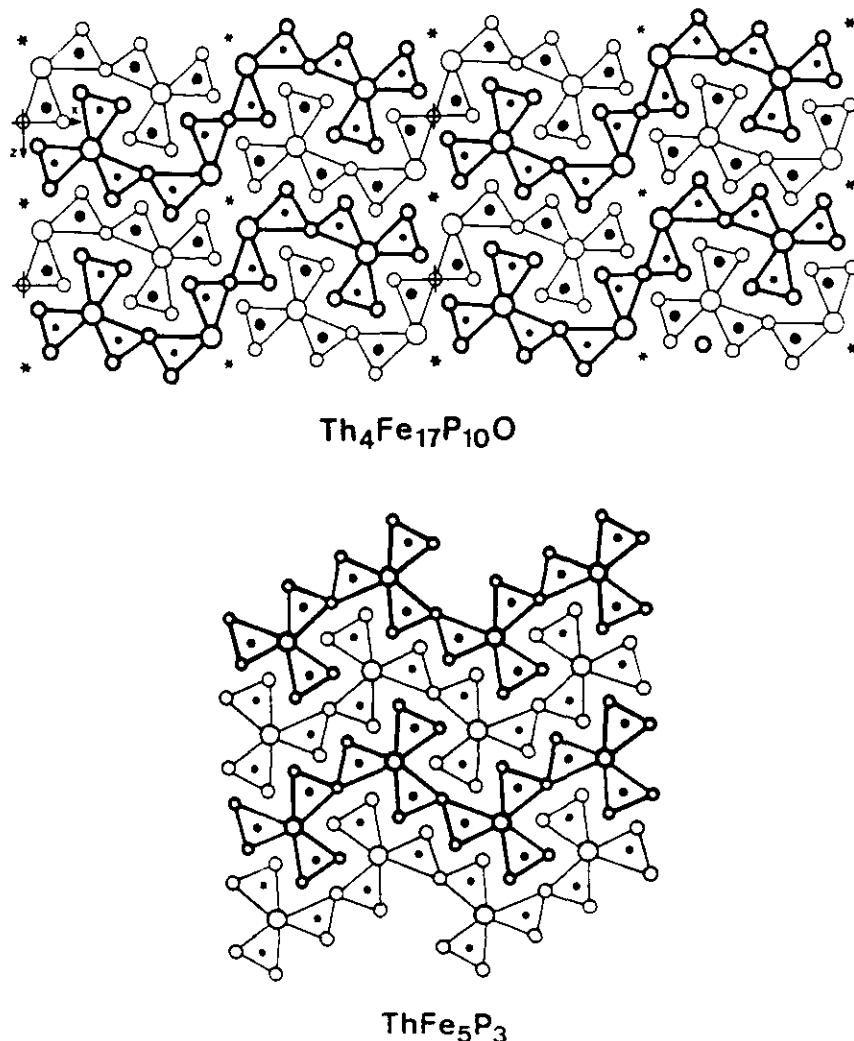


FIG. 2. The linkages of the trigonal metal prisms in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ and ThFe_5P_3 . Atoms connected by thin and thick lines are separated by half a translation period of the projection direction. Large and small open circles represent Th and Fe atoms. P and O atoms are shown as filled circles and stars, respectively.

P neighbors in square-pyramidal arrangement. The average Fe3–P distance of 255 pm is much longer than the average Fe–P distance of the tetrahedral iron atoms, as could be expected. The Fe9 atom has four P neighbors forming a rectangle. This rarely observed coordination is also present for two iron sites of $\text{Th}_5\text{Fe}_{19}\text{P}_{12}$ (6). Finally, the Fe8 atom has one oxygen and three P neighbors in a (distorted) tetrahedral arrangement.

There are numerous Fe–Fe interactions with distances ranging from 238 (Fe1–Fe9) to 289 pm (Fe3–Fe4). Certainly for the shorter ones strong iron–iron bonding can be assumed. The near neighbor distance in the ccp (γ) modification of elemental iron is 258 pm (31). In Fig. 3 we

show the arrangement of the iron atoms in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ and ThFe_5P_3 together with the arrangement of the transition metals in closely related structures. The metal–metal bonds shorter than 270 (Fe–Fe) and 275 pm (Cr–Cr, Co–Co, Ni–Ni) are also shown. There are Fe–Fe distances greater than these somewhat arbitrarily chosen cutoffs, and up to the Fe3–Fe4 distance of 288.7(3) pm, occurring in $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$, they might be considered as at least weakly bonding. The cutoffs of 270 and 275 pm, respectively, were chosen to emphasize similar building blocks, which are common in these structures, as can be seen from Fig. 3. It remains to be seen whether it is useful to classify these structures according to the kind of metal–metal bonding.

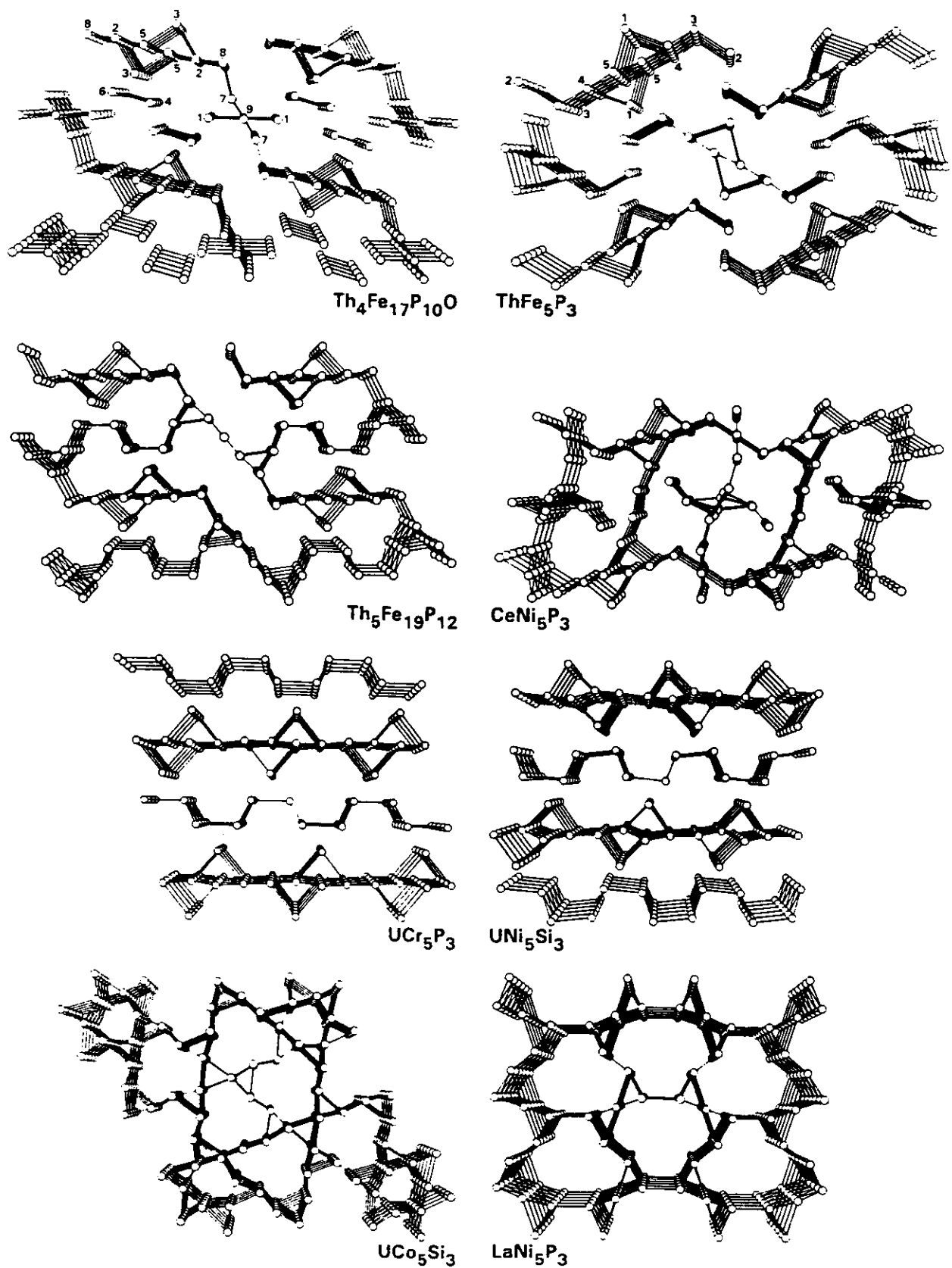


FIG. 3. The arrangement of the transition metal atoms in the structures of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$, ThFe_5P_3 , $\text{Th}_5\text{Fe}_{19}\text{P}_{12}$ (6), CeNi_5P_3 (32), UCr_5P_3 (19), UNi_5Si_3 (33), UCo_5Si_3 (34), and LaNi_5P_3 (35, 36). All Fe-Fe distances shorter than 270 pm and all Cr-Cr, Ni-Ni, and Co-Co bonds shorter than 275 pm are shown. The numbers in the drawings of $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}$ and ThFe_5P_3 correspond to the atom designations.

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