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Synthesis and Crystal Structure of a New Series of Ternary Phosphides in the Systems *Tr*–Co–P (*Tr*: Rare Earth)

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The new compounds $Tr_xCo_4P_{12}$ were prepared by reaction of the elemental components in molten Sn for Tr = La, Ce, Pr, Nd, Yb. The structure of $La_{0.2}Co_4P_{12}$ and $Ce_{0.25}Co_4P_{12}$ was refined from single-crystal data. It represents an intermediate structural type between the skutterudite and the structure reported recently by Jeitschko for $LaFe_4P_{12}$.

Introduction

Binary skutterudite-type compounds are formed with all nine possible combinations of the elements Co, Rh, Ir with P, As, and Sb (*1*). The corresponding phases with iron or ruthenium and osmium do not exist. However, it has been reported recently (*2*) that new series of rare earth ternary phosphides with general formula TrM_4P_{12} (*Tr*: rare earth; *M*: Fe, Ru, Os) exist in a body-centered cubic structure which can be described as a filled skutterudite one where the two icosahedral voids at (0 0 0) and ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) are filled with the rare earth atoms.

An examination of the system *Tr*–Co–P in the same range of composition reveals the presence of some phases $Tr_xCo_4P_{12}$ isotypic with the previously reported $TrFe_4P_{12}$.

In this paper we report on the synthesis, the crystal growth, and the crystal structure refinement of this new series of ternary phosphides.

Experimental

Samples were prepared from elemental components (all of purity > 99.5%) using liquid tin as a reaction medium.

This method was already used to synthesize transition metal phosphides (*3*, *4*) and ternary rare earth transition metal phosphides. The elements were in the atomic ratio 1 : 4 : 12 and the tin contents of the mixtures varied between 80 and 85 wt%. The mixtures were sealed in silica tubes under vacuum and heated for 2 days at 1300 K. After slow cooling (3 K/hr) to 800 K, the

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samples were quenched in water. The resulting mixtures were treated electrochemically to eliminate the Sn matrix. The resulting crystals of "$Tr_xCo_4P_{12}$" have cubic habit with dimensions up to 1.00 mm.

Seemann-Bohlin powder patterns of ground crystals were recorded with Si as standard. Cell constants were refined by least-squares calculations. The a parameters of the crystals obtained are listed in Table I. The comparison of these parameters with that of CoP_3 give the first indication of the incorporation of the rare earth in the skutterudite lattice only in the case of La, Ce, Pr, Nd, and Yb. This is confirmed by energy-dispersive analysis using a scanning electron microscope which gives an approximate composition: $Tr_{0.5}Co_4P_{12}$ for these phases, without any inclusion of tin (delectability limit on the order of 1%).

Structure Refinement

A single crystal of $Ce_xCo_4P_{12}$ was isolated from a sample prepared as described above. It had over all dimensions of about (0.11 × 0.09 × 0.09) mm and was chosen for photographic study and intensity measurements.

Preliminary precession photographs confirmed the cubic symmetry and parameter found by powder methods. Cell parameter was determined by least-squares refinement of 20 reflexions aligned on a 4-circle diffractometer; the following value was obtained: $a = 7.738(2)$ Å, $V = 463.3(4)$ Å^3, $F(000) = 692$, $Z = 2$, $D_c = 5.358$ g · cm^{-3}, $\mu(\text{Mo}K\alpha) = 141.205$ cm^{-1}.

Intensities were recorded on the same crystal mounted on an on-line Nonius CAD4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation (0.710 Å). The exploration of the half sphere of reflexion in the interval: $0 < \theta < 35°$; $-11 < h < 11$, $-11 < k < 11$, $0 < l < 11$ allowed to collect and measure 2157 reflexions. The conditions of measurement are as follows: the ω-scan mode was used with scan speed of 0.04° sec^{-1} and scan width was varied as $\Delta\omega = 1.3 \pm 0.01$ tg θ, where θ is the Bragg angle; three standard reflexions (800, 080, 008) were examined every 200 reflexions to check on the crystal alignment. The variation observed in the intensities of these three reflexions required correction less than 1% throughout the data collection.

Raw intensities are corrected for Lorentz-polarization factor and anisotropic absorption; reflexions were averaged ($R_{\text{int}} = 4.2\%$). The structure was refined in space group $Im3$ with Ce, Co, P in the positions 2(a), 8(c), and 24(g), respectively. The initial parameters for the P positions were taken as obtained for the P positions in La Fe_4P_{12} (2). Scattering factors for neutral at-

TABLE I

CELL DIMENSION OF RARE EARTH METAL COBALT PHOSPHIDES

	a (Å)	
	Single crystal (Mo$K\alpha$)	Powder method (Cr$K\alpha_1$)
$La_xCo_4P_{12}$	7.745(2)	7.735(4)
$Ge_xCo_4P_{12}$	7.738(2)	7.732(3)
$Pr_xCo_4P_{12}$	^{a}	7.733(3)
$Nd_xCo_4P_{12}$	^{a}	7.723(3)
$Yb_xCo_4p_{12}$	^{a}	7.718(1)
CoP_3		7.706(4)

[a] Crystals under investigation.

TABLE IIa

POSITIONAL AND THERMAL PARAMETERS OF $La_{0.2}Co_4P_{12}$

	La	Co	P
$Im3$	2(a)	8(c)	24(g)
x	0	$\frac{1}{4}$	0
y	0	$\frac{1}{4}$	0.3503(1)
z	0	$\frac{1}{4}$	0.1455(1)
β_{11}	0.0018(5)	0.0012(1)	0.0014(1)
β_{22}	β_{11}	β_{11}	0.0025(1)
β_{33}	β_{11}	β_{11}	0.0016(1)
β_{12}	0	0.0001(3)	0
β_{13}	0	β_{12}	0
β_{23}	0	β_{12}	0.004(2)
B_{eq}	0.46(5)	0.289(2)	0.44(1)
Occup fact	0.20(1)	4.00	12.00

TABLE IIb

POSITIONAL AND THERMAL PARAMETERS OF $Ce_{0.25}Co_4P_{12}$

	Ce	Co	P
*Im*3	2(*a*)	8(*c*)	24(*g*)
x	0	$\frac{1}{4}$	0
y	0	$\frac{1}{4}$	0.35060(1)
z	0	$\frac{1}{4}$	0.14571(7)
β_{11}	0.0022(2)	0.00130(6)	0.00148(6)
β_{22}	β_{11}	β_{11}	0.00250(6)
β_{33}	β_{11}	β_{11}	0.00168(6)
β_{12}	0	0.0001(2)	0
β_{13}	0	β_{12}	0
β_{23}	0	β_{12}	0.0005(1)
B_{eq}	0.55(2)	0.302(7)	0.445(8)
Occup fact	0.25(1)	4.00	12.00

Notes. Standard deviations in the least significant digits are given in parentheses. Anisotropic thermal parameters are defined by $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Equivalent isotropic parameters $B_{eq} = \frac{4}{3}\,\Sigma\beta_{ij}a_ia_j$ are in Å^2.

oms were used (*8*), corrected for anomalous dispersion (*9*). The weighting scheme was $w = 1$. A final refinement using anisotropic temperature factors for all atoms converged to $R = 1.4\%$ and $R_w = 1.7\%$ ($R_w = [\Sigma_w(|F_0| - |kF_c|)^2/\Sigma_w F_0^2]^{1/2}$) for 176 independent reflexions, excluding 15 weak reflexions according to the criterion $F_0^2 < 3\,\sigma(F_0^2)$ and 13 others reflexions characterized by an asymmetric background. This refinement led to $x = 0.25$ in $Ce_xCo_4P_{12}$.

TABLE III

POWDER PATTERN OF $La_{0.2}Co_4P_{12}$ AND $Ce_{0.25}Co_4P_{12}$ ($CrK\alpha_1$ RADIATION)

	$La_{0.2}Co_4P_{12}$			$Ce_{0.25}Co_4P_{12}$		
hkl	D_o	D_c	I_o	D_o	D_c	I_o
110	5.468(6)	5.468(5)	vw	—	5.476(5)	—
200	3.867(8)	3.866(8)	m	3.866(2)	3.866(1)	m
220	2.734(9)	2.734(3)	m	2.733(7)	2.733(8)	m
130	2.445(7)	2.445(6)	s	2.445(4)	2.445(1)	s
310						
222	2.232(7)	2.232(4)	w	2.232(4)	2.232(1)	w
321	2.067(2)	2.066(9)	w	2.066(8)	2.066(5)	m
231						
400	1.933(6)	1.933(4)	vw	1.932(8)	1.933(1)	w
330	1.822(6)	1.822(8)	vw	—	1.825(5)	—
411						
420	1.729(1)	1.729(3)	vs	1.728(7)	1.729(1)	vs
240						

A similar work led to $x = 0.2$ in $La_xCo_4P_{12}$ under approximately the same conditions.

Final positional and thermal parameters of both compounds are given in Tables IIa,b. A schematic drawing of the structure is shown in Fig. 1a. The powder patterns of $La_{0.2}Co_4P_{12}$ and $Ce_{0.25}Co_4P_{12}$ are given in Table III.

Discussion

The structure and bonding of this new series of components may be analyzed by comparison with CoP_3 and $LaFe_4P_{12}$ which have been previously discussed by

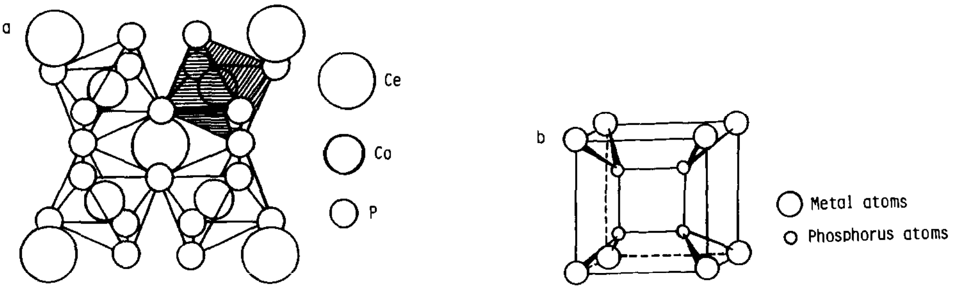

FIG. 1. (a) The body-centered cubic of $Ce_xCo_4P_{12}$. The shaded portion is a distorted corner-sharing octahedron of phosphorus atoms centered by cobalt (*10*). (b) The environment of the phosphorus atoms in the skutterudite-type structure. Four phosphorus atoms are linked into planar, rectangular groups (*5*).

TABLE IV

INTERATOMIC DISTANCES (Å) AND SELECTED INTERATOMIC ANGLES (°)[a]

	CoP_3[b]	$LaFe_4P_{12}$[c]	$La_{0.2}Co_4P_{12}$	$Ce_{0.25}Co_4P_{12}$
		Distances		
Tr–P		3.012[12×]	2.938(2)[12×]	2.938(1)[12×]
Tr–*M*		3.391[8×]	3.354(2)[8×]	3.351(2)[8×]
M–P	2.22(2)[6×]	2.259[6×]	2.238(1)[6×]	2.236(1)[6×]
P–*M*		2.259[2×]	2.238(1)[2×]	2.236(1)[2×]
M–Tr		3.391[2×]	3.354(2)[2×]	3.351(2)[2×]
P–*Tr*		3.012[2×]	2.938(2)[2×]	2.938(1)[2×]
P–P′	2.24(0)[1×]	2.288[1×]	2.254(2)[1×]	2.255(2)[1×]
P–P″	2.34(0)[1×]	2.356[1×]	2.319(2)[1×]	2.312(2)[1×]
P–P		2.968[4×]	2.980(2)[4×]	2.975(2)[4×]
P–P		3.284[1×]	3.234(2)[1×]	3.229(2)[1×]
P–P		3.407[1×]	3.339(2)[1×]	3.338(2)[1×]
		Angles		
P–*M*–P		180.0[3×]	179.19(4)[3×]	179.19(3)[3×]
P–*M*–P	84.0[6×]	82.1[6×]	83.51(4)[6×]	83.42(2)[6×]
P–*M*–P	96.0[6×]	97.9[6×]	96.49(4)[6×]	96.58(4)[6×]
P′–P–P″		90.0[1×]	90.00(4)[1×]	90.00(2)[1×]
M–P–*M*	120.3[1×]	120.0[1×]	119.84(5)[1×]	119.81(3)[1×]
M–P–P′	109.9[2×]	110.2[2×]	110.31(5)[2×]	110.38(4)[2×]
M–P–P″	111.3[2×]	111.1[2×]	111.20(5)[2×]	111.16(3)[2×]
Tr–P–P′		157.0[1×]	157.44(5)[1×]	157.43(4)[1×]
Tr–P–P″		67.0[1×]	67.44(4)[1×]	67.43(3)[1×]
Tr–P–*M*		78.7[2×]	79.52(4)[2×]	79.46(3)[2×]

[a] All distances shorter than 3.5 Å are listed.

[b] Standard deviations in the angles are not provided by literature.

[c] Standard deviations are all less than 0.002 Å and 0.1° (*2*).

Rundqvist (*5*), Kjekshus (*7*), and Jeitschko (*2*). For this purpose we have listed in Table IV all interatomic distances for both compounds together with those for $La_{0.2}Co_4P_{12}$ and $Ce_{0.25}Co_4P_{12}$. The general atomic arrangement in the skutterudite-type structure can be described as an infinite three-dimensional array of a distorted MeX_6 octahedron sharing corners with six neighboring octahedra. Two points are important: the degree of distortion of the MeX_6 octahedron and the environment of the nonmetal atom. Each nonmetal atom has four near neighbors: two metal and two nonmetal atoms arranged at the corners of a distorted tetrahedron (Fig. 1b). The nonmetal atoms cluster in groups of four in a X_4 planar rectangular arrangement. The structural environment of the nonmetal atom is completely determined by the two positional parameters y and z for this atom. The three distances of interest are given by the following equations:

$$d(Me\text{–}X) = a((\tfrac{1}{4})^2 + (y - \tfrac{1}{4})^2 + (z - \tfrac{1}{4})^2)^{1/2}$$

$$d_1(X\text{–}X) = a2z$$

$$d_2(X\text{–}X) = a \cdot (1 - y).$$

The Oftedal relation $y + z = \frac{1}{2}$ (*6*) which indicates that the X–X distances along the edges of the X_4 group are equal is valid only if $d_1 = d_2$. For CoP_3 it was found that $y + z$ deviates significantly from $\frac{1}{2}$. In the new compounds $La_{0.2}Co_4P_{12}$ and $Ce_{0.25}Co_4P_{12}$ the relation is still not satisfied but to a lesser extent.

As pointed out previously by Rundqvist (*5*), for an ideal octahedral coordination around the metal atoms, the parameters y and z must satisfy the relation $8 \cdot y\,(2 \cdot z - 1) = 8 \cdot z - 3$. The y and z values for $La_{0.2}Co_4P_{12}$ and $Ce_{0.25}Co_4P_{12}$ indicate that the CoP_6 octahedron is more distorted in these phases than in CoP_3. Like in $LaFe_4P_{12}$ the icosahedral voids of the Co_4P_{12} framework are too small and the deviations from ideal octahedral P–Fe–P angles are such that more room is obtained for the large Tr^{3+} ion. This effect is less pronounced in the *Tr*–Co phosphides than in the corresponding *Tr*–Fe phosphides in agreement with the degree of occupancy of the icosahedral voids. This distortion must be considered as the consequence of the rare earth introduction in the lattice but cannot explain the formula obtained for these compounds. By changing the initial ratio *Tr* : Co : P in the tin melt we obtained always the same parameters, which indicates a small homogeneity range for these compounds.

Work is in progress by X-ray diffraction and electron microscopy for the purpose of detecting eventual superstructures which may explain the degree of occupancy of the rare earth sites in these phases.

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