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Ternary Lanthanoid Iron Phosphides with YCo_5P_3 and $Zr_2Fe_{12}P_7$-Type Structures

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The new compounds YFe_5P_3 and $LnFe_5P_3$ (Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were prepared by reaction of the elemental components in a tin flux. They have YCo_5P_3-type structure. A structure refinement of $GdFe_5P_3$ from single-crystal X-ray data resulted in a conventional residual of $R = 0.063$ for 29 variable parameters and 693 unique structure factors. Crystals of the new compound $Ce_2Fe_{12}P_7$ were also prepared by the tin flux technique. Their $Zr_2Fe_{12}P_7$-type structure was refined to $R = 0.029$ for 23 variables and 1365 F values. The coordination polyhedra of the two and some other closely related structure types are discussed. The thermal parameters of the transition metal atoms in such structures increase with increasing coordination number.

Introduction

In previous investigations ternary lanthanoid iron phosphides were prepared with the following structure types: $LaFe_4P_{12}$ (*1*), $ThCr_2Si_2$ (*2*), and $Zr_2Fe_{12}P_7$ (*3*). Recently a series of compounds with the composition $LnCo_5P_3$ (Ln = lanthanoid elements) was synthesized. They crystallize with a new structure type which was determined for YCo_5P_3 (*4*). In the search for isotypic compounds we have now investigated the iron-rich part of such ternary systems with the following results.

Sample Preparation

Filings of the rare earth metals (stated purities of 99.9%) were prepared from ingots under dried paraffin oil. They were washed with dried methylene chloride in argon and not allowed to contact air prior to sealing under vacuum for the synthesis. Iron and tin (both 99.9%) were in powder form. Red phosphorus (Merck: "rein") was boiled in NaOH solution to remove oxidation products (*5*).

The samples were prepared by the tin flux technique in evacuated sealed silica tubes. Typical starting compositions for the preparation of the YCo_5P_3-type compounds had the atomic ratios Y or Ln : Fe : P : Sn = 1 : 2 : 1 : 20. The samples were annealed for 7 days at 850°C and quenched. The tin-rich matrix was dissolved in hydrochloric acid (1 : 1) which does not attack the ternary compounds. Energy dispersive analyses of the black, needle-shaped crystals in a scanning electron microscope showed no impurities like tin or silicon (2% detectability limits).

Single-phase products of the new com-

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pound $Ce_2Fe_{12}P_7$ were obtained with starting compositions varying between Ce:Fe:P:Sn = 4:1:2:20, 4:2:4:20, and 2:4:4:20 with annealing for 7 days at 800°C. In other samples the compound was in equilibrium with FeP and FeP_2. CeP could also have been present, however, this compound dissolves during the hydrochloric acid treatment. Crystals of $Ce_2Fe_{12}P_7$ were also prepared in alumina containers. This excludes the possibility of Si being necessary to stabilize the compound.

Lattice Constants

X-Ray powder diffraction patterns of the products were recorded with Cu$K\alpha_1$ radiation in a Guinier camera using α-quartz (a = 4.9130 Å, c = 5.4046 Å) as reference material. To ensure proper indexing, the powder intensities were calculated (*6*) using the positional parameters as obtained in the presently reported structure refinements. The lattice constants were computed by least-squares fits of the data. It should be emphasized that the true lattice constants, thus obtained from the powder data, are always slightly greater than those calculated by the usual least-squares fits of the single-crystal diffractometer data. The systematic errors in the single-crystal diffractometer data are due to absorption effects which shift the diffracted beams to slightly higher angles. The hexagonal lattice constants of $Ce_2Fe_{12}P_7$ are a = 9.135(2) Å, c = 3.677(1) Å, c/a = 0.4025, V = 265.7 Å^3. The lattice constants of the new YCo_5P_3-type compounds are listed in Table I. As an example the first lines of the evaluation of the powder pattern of $TmFe_5P_3$ are shown in Table II.

Structure Refinements of $Ce_2Fe_{12}P_7$ and $GdFe_5P_3$

Single crystals of $Ce_2Fe_{12}P_7$ were examined in a Weissenberg camera. The patterns

TABLE I

CELL DIMENSIONS OF COMPOUNDS WITH ORTHORHOMBIC YCo_5P_3-TYPE STRUCTURE[a]

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)
YFe_5P_3	12.008(3)	3.672(1)	10.423(3)	459.6(2)
$GdFe_5P_3$	12.043(3)	3.683(1)	10.460(3)	464.0(2)
$TbFe_5P_3$	12.013(2)	3.675(1)	10.436(1)	460.7(1)
$DyFe_5P_3$	11.999(3)	3.666(1)	10.423(2)	458.5(1)
$HoFe_5P_3$	11.988(2)	3.663(1)	10.410(2)	457.1(1)
$ErFe_5P_3$	11.976(2)	3.657(1)	10.400(1)	455.5(1)
$TmFe_5P_3$	11.965(3)	3.652(1)	10.392(3)	454.1(1)
$YbFe_5P_3$	11.954(2)	3.647(1)	10.378(1)	452.4(1)
$LuFe_5P_3$	11.948(2)	3.643(1)	10.372(2)	451.4(1)

[a] Standard deviations in the least-significant digits are given in parentheses.

TABLE II

POWDER PATTERN OF $TmFe_5P_3$ WITH YCo_5P_3-TYPE STRUCTURE[a]

hkl	Q_c	Q_0	I_c	I_0
101	162	—	<1	—
200	279	280	5	vw
002	370	—	4	—
201	372	372	12	w
102	440	—	<1	—
202	649	—	1	—
301	721	710	6	vw
011	842	840	8	vw
103	903	—	<1	—
111	912	912	20	m
302	999	1001	16	w
210	1029	1027	6	w
203	1113	1109	27	m
400	1117	—	3	—
211	1121	—	3	—
112	1189	—	4	—
401	1210	—	3	—
212	1399	—	<1	—
303	1462	—	<1	—
311	1470	1468	6	vw
004	1481	—	2	—
402	1488	—	<1	—
104	1551	1552	10	w
013	1583	1582	28	w
113	1653	—	1	—
312	1749	1747	13	w
204	1761	—	4	—
501	1839	1841	14	vw
213	1862	1864	100	vs
410	1867		62	

TABLE II—*Continued*

hkl	Q_c	Q_0	I_c	I_0
403	1951	1957	13	w
411	1960		6	
304	2110	2110	15	w
502	2117	—	2	—
313	2212	—	<1	—
412	2238	—	4	—
114	2301	2302	7	w
105	2385	2384	9	w
214	2510	2508	5	w
600	2515	—	3	—
503	2580	—	2	—
511	2589	2585	4	vw
205	2594	—	2	—
404	2599	—	2	—
601	2607	—	1	—
413	2701	—	8	—
314	2861	2863	6	w
512	2866	—	1	—
602	2884	—	4	—
305	2944	—	2	—
020	3000	3001	39	vs

[a] The Q values are defined by $Q = 10^4/d^2$ (Å^{-2}).

showed $6/m$ symmetry and no systematic extinctions. Thus the space groups $P6$, $P\bar{6}$, and $P6/m$ were possible of which $P\bar{6}$ was found to be correct during the structure refinement.

The crystals of $GdFe_5P_3$—examined in a Buerger camera—have Laue symmetry *mmm* with the following conditions for observed reflections: $0kl$ only with $k + l = 2n$ and $hk0$ only with $h = 2n$. These indicate the space groups *Pnma* and $Pn2_1a$. The structure refinements gave no reason for the lower symmetry group. Thus the centrosymmetric group *Pnma* is correct.

Intensity data for both compounds were collected in a four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. Scans were recorded along θ with background counts at both ends of each scan. The scan rates were variable and the optimal rate for each scan was determined by a fast prescan. Empirical absorption corrections were made from psi scan data.

A total of 4895 reflections were measured for the $Ce_2Fe_{12}P_7$ crystal within one-half of the reciprocal sphere up to $2\theta = 90°$. After averaging of equivalent reflections and omitting those with intensities of less than two standard deviations 1365 reflections remained which were used for the structure refinements. For the $GdFe_5P_3$ crystal one set of unique reflections was measured up to $2\theta = 80°$. Of the total of 1706 reflections 693 remained after omitting all reflections with intensities less than 5σ.

The isotypy of $Ce_2Fe_{12}P_7$ and $GdFe_5P_3$ with $Zr_2Fe_{12}P_7$ (*7*) and YCo_5P_3 (*4*), respectively, was recognized already from the powder patterns. For the full matrix least-squares structure refinements scattering factors for neutral atoms (*8*) were used, corrected for anomalous dispersion (*9*). The weighting schemes were according to the counting statistics. Isotropic extinction parameters were refined and applied to the F_c values.

We have also refined occupancy parameters to possibly obtain indications for deviations from the ideal compositions. The results for $GdFe_5P_3$ were: Gd, 100.7 ± 1.0%; for the Fe(1) to Fe(5) positions, 99.7, 100.6, 101.1, 99.0, and 99.4% with standard deviations of 1.7%; for the P positions, 95.4, 100.3, and 97.7% with standard deviations of 2.9%. For $Ce_2Fe_{12}P_7$ the refined occupancy parameters were even closer to the ideal values: Ce(1) and Ce(2), 100.1 and 100.3% ± 0.2%; for the Fe positions, 100.6, 100.0, 99.8, and 99.5 ± 0.4%; and for the P(1), P(2), and P(3) positions, 101.0 ± 0.7, 98.8 ± 0.7, and 100.4 ± 1.2%. Thus any substantial deviations from the ideal occupancies can be ruled out and we have preferred to fix the occupancy parameters to the ideal values in the last refinement cycles. The final residuals and weighted residuals are $R = 0.063$ and $R_w = 0.057$ for

$GdFe_5P_3$ (29 variable parameters and 693 structure factors), and $R = 0.029$, $R_w = 0.032$ for $Ce_2Fe_{12}P_7$ (23 variables, 1365 F values). The final parameters are listed in Table III, interatomic distances in Table IV. Listings of observed and calculated structure factors can be obtained from the authors.

Discussion

The crystal structures and structural relationships of YCo_5P_3, $Zr_2Fe_{12}P_7$, and other closely related structure types were discussed recently (*4, 10*). Compounds with the $Zr_2Fe_{12}P_7$ and YCo_5P_3 type structures have similar stoichiometries and occur in related systems. They thus compete thermodynamically with each other. Nevertheless they occur together in most of the ternary systems lanthanoid–iron,cobalt–phosphorus. With the presently reported compound $Ce_2Fe_{12}P_7$, phosphides with

TABLE III

POSITIONAL AND THERMAL PARAMETERS OF $GdFe_5P_3$ AND $Ce_2Fe_{12}P_7$[a]

$GdFe_5P_3$	*Pnma*	*x*	*y*	*z*	*B* (Å²)
Gd	4*c*	0.2051(1)	$\frac{1}{4}$	0.9182(1)	0.20(2)
Fe(1)	4*c*	0.4868(3)	$\frac{1}{4}$	0.7935(3)	0.40(5)
Fe(2)	4*c*	0.9915(3)	$\frac{1}{4}$	0.0935(4)	0.40(5)
Fe(3)	4*c*	0.6765(3)	$\frac{1}{4}$	0.2819(3)	0.31(5)
Fe(4)	4*c*	0.1972(3)	$\frac{1}{4}$	0.6230(3)	0.32(5)
Fe(5)	4*c*	0.4344(3)	$\frac{1}{4}$	0.0368(3)	0.21(4)
P(1)	4*c*	0.6142(5)	$\frac{1}{4}$	0.0786(7)	0.32(8)
P(2)	4*c*	0.3693(5)	$\frac{1}{4}$	0.2325(6)	0.27(8)
P(3)	4*c*	0.8903(5)	$\frac{1}{4}$	0.9008(6)	0.40(9)
$Ce_2Fe_{12}P_7$	$P\bar{6}$				
Ce(1)	1*c*	$\frac{1}{3}$	$\frac{2}{3}$	0	0.29(1)
Ce(2)	1*f*	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	0.31(1)
Fe(1)	3*j*	0.4297(1)	0.0589(1)	0	0.35(1)
Fe(2)	3*j*	0.1534(1)	0.2735(1)	0	0.29(1)
Fe(3)	3*k*	0.3820(1)	0.4334(1)	$\frac{1}{2}$	0.34(1)
Fe(4)	3*k*	0.2198(1)	0.0994(1)	$\frac{1}{2}$	0.43(1)
P(1)	3*j*	0.4083(2)	0.2979(2)	0	0.36(2)
P(2)	3*k*	0.1107(2)	0.4019(2)	$\frac{1}{2}$	0.42(2)
P(3)	1*a*	0	0	0	0.48(3)

[a] Standard deviations in the least-significant digits are given in parentheses.

TABLE IV

INTERATOMIC DISTANCES IN $GdFe_5P_3$ AND $Ce_2Fe_{12}P_7$[a]

$GdFe_5P_3$			$Ce_2Fe_{12}P_7$		
Gd	2 P(2)	2.823	Ce(1)	6 P(2)	2.907
	2 P(1)	2.852		6 Fe(3)	3.011
	2 P(3)	2.881		3 Fe(2)	3.113
	2 Fe(2)	3.002		3 Fe(1)	3.234
	1 Fe(5)	3.027		2 Ce(1)	3.677
	2 Fe(4)	3.060	Ce(2)	6 P(1)	2.878
	1 Fe(4)	3.089		6 Fe(1)	2.988
	2 Fe(3)	3.131		3 Fe(3)	3.158
	1 Fe(3)	3.156		3 Fe(4)	3.537
	1 Fe(2)	3.159		2 Ce(2)	3.677
	1 Fe(1)	3.438	Fe(1)	1 P(1)	2.286
	1 Fe(1)	3.634		1 P(1)	2.290
	2 Gd	3.683		2 P(2)	2.328
Fe(1)	1 P(3)	2.341		1 Fe(2)	2.504
	2 P(2)	2.544		2 Fe(3)	2.687
	2 P(1)	2.580		2 Fe(4)	2.811
	1 Fe(5)	2.621		2 Ce(2)	2.988
	1 Fe(4)	2.681		1 Ce(1)	3.234
	2 Fe(5)	2.728	Fe(2)	1 P(3)	2.170
	2 Fe(2)	2.800		1 P(1)	2.226
	2 Fe(3)	2.807		2 P(2)	2.316
	1 Gd	3.438		1 Fe(1)	2.504
	1 Gd	3.634		2 Fe(3)	2.612
Fe(2)	2 P(3)	2.328		2 Fe(4)	2.691
	1 P(2)	2.341		2 Fe(4)	2.728
	1 P(3)	2.356		1 Ce(1)	3.113
	1 Fe(3)	2.581	Fe(3)	1 P(2)	2.293
	2 Fe(2)	2.694		2 P(1)	2.296
	2 Fe(1)	2.800		1 P(2)	2.348
	2 Gd	3.002		2 Fe(2)	2.612
	1 Gd	3.159		1 Fe(4)	2.643
Fe(3)	1 P(1)	2.256		2 Fe(1)	2.687
	1 P(2)	2.326		2 Ce(1)	3.011
	2 P(3)	2.363		1 Ce(2)	3.158
	1 Fe(2)	2.581	Fe(4)	1 P(2)	2.315
	2 Fe(4)	2.587		2 P(3)	2.532
	2 Fe(1)	2.807		2 P(1)	2.552
	2 Gd	3.131		1 Fe(3)	2.643
	1 Gd	3.156		2 Fe(2)	2.691
Fe(4)	2 P(2)	2.312		2 Fe(2)	2.728
	1 P(1)	2.333		2 Fe(1)	2.811
	1 P(3)	2.339		2 Fe(4)	3.016
	2 Fe(3)	2.587		1 Ce(2)	3.537
	2 Fe(5)	2.591	P(1)	1 Fe(2)	2.226
	1 Fe(1)	2.681		1 Fe(1)	2.286
	2 Gd	3.060		1 Fe(1)	2.290
	1 Gd	3.089		2 Fe(3)	2.296
Fe(5)	1 P(2)	2.192		2 Fe(4)	2.552
	1 P(1)	2.209		2 Ce(2)	2.878

TABLE IV—*Continued*

$GdFe_5P_3$			$Ce_2Fe_{12}P_7$		
	2 P(1)	2.278	P(2)	1 Fe(3)	2.293
	2 Fe(5)	2.546		1 Fe(4)	2.315
	2 Fe(4)	2.591		2 Fe(2)	2.316
	1 Fe(1)	2.621		2 Fe(1)	2.328
	2 Fe(1)	2.728		1 Fe(3)	2.348
	1 Gd	3.027		2 Ce(1)	2.907
P(1)	1 Fe(5)	2.209	P(3)	3 Fe(2)	2.170
	1 Fe(3)	2.256		6 Fe(4)	2.532
	2 Fe(5)	2.278			
	1 Fe(4)	2.333			
	2 Fe(1)	2.580			
	2 Gd	2.852			
P(2)	1 Fe(5)	2.192			
	2 Fe(4)	2.312			
	1 Fe(3)	2.326			
	1 Fe(2)	2.341			
	2 Fe(1)	2.544			
	2 Gd	2.823			
P(3)	2 Fe(2)	2.328			
	1 Fe(4)	2.339			
	1 Fe(1)	2.341			
	1 Fe(2)	2.356			
	2 Fe(3)	2.363			
	2 Gd	2.881			

[a] Standard deviations for the distances in $GdFe_5P_3$ are all less or equal 0.005 (Gd–P), 0.004 (Gd–Fe), 0.008 (Fe–P), and 0.005 Å (Fe–Fe); for $Ce_2Fe_{12}P_7$ they are all less or equal 0.001 Å. All distances are listed which are shorter than 3.75 Å (coordination of Gd and Ce), 3.5 Å (Fe–Fe), and 3.3 Å (Fe–P and P–P).

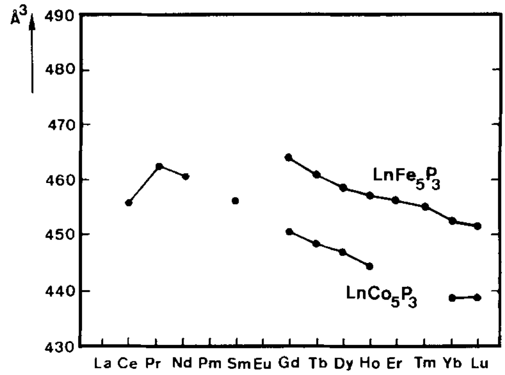

FIG. 1. Cell volumes of YCo_5P_3-type compounds.

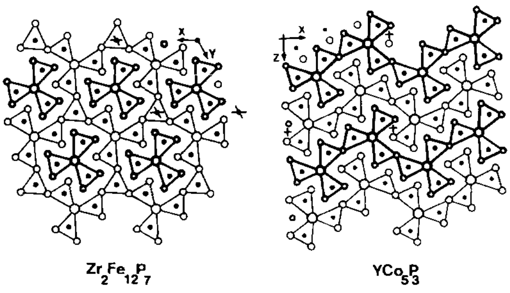

FIG. 2. Linkage of the P-containing trigonal prisms in the $Zr_2Fe_{12}P_7$- and YCo_5P_3-type structures. Atoms connected by thin and thick lines are separated by half a translation period in the projection direction. Large circles: Zr, Y; small circles: Fe, Co; filled circles: P.

$Zr_2Fe_{12}P_7$-type structure are known now for all the lanthanoids in combination with iron and cobalt with the exceptions of the La and Pm compounds and $Eu_2Fe_{12}P_7$. While the preparation of compounds with radioactive Pm was not attempted, the La compounds were not obtained, apparently because they lack stability with the large La atoms: In $LaCo_5P_3$, a third competing structure (*11*), the La atoms have a higher coordination number (CN). Irregardless of which of the usual concepts one accepts to count CNs, the CN of the rare earth metal atoms is still lower in the YCo_5P_3-type compounds. This may explain why we were not successful in preparing the iron-containing YCo_5P_3-type compounds with the early lanthanoids. The volume plot (Fig. 1) shows that Yb is trivalent in these compounds.

The environment of the P atoms in the YCo_5P_3- and $Zr_2Fe_{12}P_7$-type structures is a trigonal prism of metal atoms augmented by three additional metal neighbors outside the rectangular faces of the prism. This is the usual coordination of the P atoms in phosphides with high metal content (*12*, *13*). In emphasizing this coordination the similarity of the two structures is obvious (Fig. 2).

The environments of the transition metal atoms are less uniform. The Fe(1) atoms of $GdFe_5P_3$ and the Fe(4) atoms of $Ce_2Fe_{12}P_7$ have five P neighbors forming a somewhat distorted square pyramid with 9 or 10 (depending on whether one counts the Fe(4)–Ce(2) interaction of 3.537 Å) additional metal neighbors (CN = 15). The other Fe atoms have distorted tetrahedral P coordination with eight additional metal atoms (CN = 12). Similar coordination polyhedra were already observed for the transition metal atoms in the TiNiSi (*14*) and TiCoGe (*15*) type structures, where the corresponding sites are sometimes referred to as "pyramidal" and "tetrahedral" (*16, 17*).

It is interesting that in the structure refinements of $GdFe_5P_3$ and $Ce_2Fe_{12}P_7$ the iron atoms at the tetrahedral sites with the small CN = 12 have smaller thermal parameters B than the iron atoms of the pyramidal sites with the larger CNs. This seems to be generally true for metal atoms of one and the same kind with greatly differing CNs. Other examples can be found in the structure refinements of $Er_2Co_{12}P_7$ and $Er_2Ni_{12}P_7$ (*10*), $Nb_6Ni_6P_9$ (*18*), YCo_5P_3 (*4*), and La Co_8P_5 (*19*). With very small CNs the opposite can be observed. Thus for instance in the structures of β-$SnWO_4$ (*20*) and $La_2(MoO_4)_3$ (*21*) the two-coordinated oxygen atoms have larger thermal parameters than the three-coordinated ones.

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