

## Lanthanoid-Nickel-Phosphides with $\text{ThCr}_2\text{Si}_2$ -Type Structure

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The new compounds  $\text{YNi}_2\text{P}_2$  and  $\text{LnNi}_2\text{P}_2$  ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm}$ ) were prepared by sintering the elemental components in silica tubes. Well-developed crystals were obtained using tin as a flux. They crystallize with the  $\text{ThCr}_2\text{Si}_2$  ( $\text{CeGa}_2\text{Al}_2$ )-type structure which was refined from single-crystal X-ray data for  $\text{EuNi}_2\text{P}_2$  to a conventional  $R$  value of 0.049 for 118 unique structure factors. While the P atoms in formally isotypic  $\text{EuCo}_2\text{P}_2$  are isolated from each other, they form pairs in  $\text{EuNi}_2\text{P}_2$ . This results in a different  $c/a$  ratio and an entirely different bonding situation. A comparison of cell volumes shows that Eu in  $\text{EuNi}_2\text{P}_2$  has an intermediate valence.

### Introduction

Almost 300 silicides and germanides with the composition  $\text{AB}_2\text{X}_2$  ( $A =$  earth and rare earth metals, actinoids;  $B =$  transition and posttransition metals;  $X = \text{Si, Ge}$ ) are known to crystallize with the  $\text{ThCr}_2\text{Si}_2$ -type structure (1-25). Only very recently several corresponding compounds were reported where the  $X$  component is a pnictogen element (P, As, Sb):  $\text{CaNi}_2\text{P}_2$  (26),  $\text{CaCu}_2\text{P}_2$  (27),  $\text{BaZn}_2\text{P}_2$  (28),  $\text{BaMn}_2\text{P}_2$  (29),  $\text{BaMn}_2\text{As}_2$  (30). A sampling investigation (31) of similar compositions with the lanthanoids as the most electropositive component yielded 15 new compounds with that structure including  $\text{EuNi}_2\text{P}_2$ ,  $\text{GdNi}_2\text{P}_2$ , and  $\text{YbNi}_2\text{P}_2$ . We have now studied the formation of the lanthanoid-nickel phosphides with  $\text{ThCr}_2\text{Si}_2$ -type structure systematically.

It was noted earlier (31) that the  $c/a$  ratio of the Ni-containing compounds was very different from that of the compounds with Fe or Co as transition metal component. To obtain a better understanding of this unexpected behavior, we have now refined the crystal structure of  $\text{EuNi}_2\text{P}_2$  and compare it with the earlier reported structure of  $\text{EuCo}_2\text{P}_2$ .

### Experimental

Sample preparation was essentially as reported before for similar compositions (31-36). Starting materials were the elemental components with stated purities >99.5%. Filings of the rare earth elements were prepared under argon. Stoichiometric mixtures of the components in finely divided form were sealed in silica tubes under vacuum, annealed for 2 weeks at 1050 K, and then slowly cooled to room temperature within 4 days. This procedure yielded only microcrystalline products. Well crystallized materials were obtained by adding

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about 30 at% tin as a flux. The heat treatment was the same. The tin-rich matrix was dissolved in moderately diluted (1:1) hydrochloric acid, which did not greatly affect the crystals of the new compounds: electron microscopy showed them to have well-developed faces and sharp edges.

X-Ray powder diffraction patterns of the products were recorded with a Guinier camera using  $\alpha$ -quartz as standard ( $a = 4.9130$ ,  $c = 5.4046$  Å). They were indexed on the basis of the body-centered tetragonal cell and the lattice constants (Table I) were refined by a least-squares treatment of the data. Intensity calculations gave good agreement in all cases for  $\text{ThCr}_2\text{Si}_2$ -type structures. As an example the evaluation of a powder pattern for  $\text{NdNi}_2\text{P}_2$  is shown in Table II.

### Structure Refinement of $\text{EuNi}_2\text{P}_2$

Single crystals of  $\text{EuNi}_2\text{P}_2$  were examined with Buerger precession and Weissenberg cameras. The diffraction patterns show a body-centered tetragonal cell with

TABLE I  
CELL DIMENSIONS OF COMPOUNDS WITH  
 $\text{ThCr}_2\text{Si}_2$ -TYPE STRUCTURE<sup>a</sup>

	$a$ (Å)	$c$ (Å)	$c/a$	$V$ (Å <sup>3</sup> )
$\text{YNi}_2\text{P}_2$	3.859	9.332	2.418	139.0
$\text{LaNi}_2\text{P}_2$	4.007	9.632	2.404	154.6
$\text{CeNi}_2\text{P}_2$	3.955	9.505	2.403	148.7
$\text{PrNi}_2\text{P}_2$	3.952	9.493	2.402	148.3
$\text{NdNi}_2\text{P}_2$	3.942	9.461	2.400	147.0
$\text{SmNi}_2\text{P}_2$	3.919	9.403	2.399	144.4
$\text{EuNi}_2\text{P}_2$	3.938	9.469	2.404	146.8
$\text{GdNi}_2\text{P}_2$	3.892	9.372	2.408	142.0
$\text{TbNi}_2\text{P}_2$	3.870	9.342	2.414	139.9
$\text{DyNi}_2\text{P}_2$	3.857	9.332	2.419	138.8
$\text{HoNi}_2\text{P}_2$	3.844	9.329	2.427	137.9
$\text{ErNi}_2\text{P}_2$	3.830	9.303	2.429	136.5
$\text{TmNi}_2\text{P}_2$	3.823	9.310	2.435	136.1
$\text{YbNi}_2\text{P}_2$	3.834	9.323	1.432	137.0

<sup>a</sup> Standard deviations are all about  $\pm 0.002$  Å in  $a$  and  $\pm 0.006$  Å in  $c$ .

TABLE II  
GUINIER POWDER PATTERN OF  $\text{NdNi}_2\text{P}_2$  WITH  
 $\text{ThCr}_2\text{Si}_2$ -TYPE STRUCTURE<sup>a</sup>

$hkl$	$Q_0$	$Q_c$	$I_0$	$I_c$
002	—	447	—	2
101	756	755	s	40
110	1284	1287	w	9
103	1650	1649	s	57
112	1736	1734	vs	100
004	1789	1788	vw	14
200	2578	2574	s	44
202	—	3021	—	1
114	—	3075	—	2
211	3331	3329	w	12
105	3438	3437	w	20
006	—	4022	—	<1
213	Koinz.	4223	m	30
204	4356	4362	w	15
220	5144	5148	w	17
116	Koinz.	5309	w	20

<sup>a</sup> For the calculation of the powder pattern (37) the  $z$  parameter of the P position was assumed as obtained in the least-squares refinement of  $\text{EuNi}_2\text{P}_2$ .

diffraction symmetry  $4/mmm$ . No other extinctions were observed. The structure refinement gave no indication for a symmetry lower than  $I4/mmm$ .

Intensity data were collected from a crystal of square prismatic shape ( $90 \times 90 \times 120$   $\mu\text{m}^3$ ) with an automated four-circle diffractometer, monochromatized  $\text{MoK}\alpha$  radiation, scintillation counter, and pulse-height discriminator.  $\theta$ - $2\theta$  scans were taken up to  $2\theta = 80^\circ$ . Background was counted at both ends of each scan. All reflections within a quarter sphere of reciprocal space were collected and averaged, thus yielding 122 unique reflections. An absorption correction was applied, assuming spherical crystal shape.

Starting parameters for the full-matrix least-squares refinement (38) were taken as obtained for  $\text{EuCo}_2\text{P}_2$  (31). Scattering factors for neutral atoms (39) were used, corrected for anomalous dispersion (40). The weighting scheme was according to counting statistics. An isotropic parameter ac-

TABLE III  
RESULTS OF THE LEAST-SQUARES REFINEMENT OF  
THE CRYSTAL STRUCTURE OF  $\text{EuNi}_2\text{P}_2$ <sup>a</sup>

	$I4/mmm$	$x$	$y$	$z$	$B(\text{\AA}^2)$
Eu	$2a$	0	0	0	0.54(2)
Ni	$4d$	0	$\frac{1}{2}$	$\frac{1}{4}$	0.58(4)
P	$4e$	0	0	0.3748(4)	0.79(7)

<sup>a</sup> Standard deviations in the least significant digits are given in parentheses.

counting for secondary extinction was refined and applied to the calculated structure factors. A final conventional  $R$  value of 0.049 was obtained for the 118 structure factors excluding four very weak reflections. A final difference Fourier analysis resulted in no peaks higher than 4.8 or lower than  $-10.9 \text{ e}/\text{\AA}^3$ . These strong features were all in the vicinity of the heavy atom positions. The highest peaks at possible interstitial sites were all less than  $1 \text{ e}/\text{\AA}^3$ . Final parameters, a list of the structure factors, and interatomic distances are given in Tables III, IV, and V. A drawing of the structure is shown in Fig. 1.

### Discussion

The most interesting result of the present work is the great difference in near-neighbor environments in  $\text{EuNi}_2\text{P}_2$  when compared to the near-neighbor coordinations in the formally isotopic compound  $\text{EuCo}_2\text{P}_2$ . This results in an entirely different bonding situation. In  $\text{EuCo}_2\text{P}_2$  (31) the shortest P-P distance is 3.27  $\text{\AA}$  and thus certainly non-bonding. Therefore a formal oxidation number of  $-3$  can be assumed for the P atoms and bonding can formally (where shared bonding electrons are counted as belonging to the more electronegative partner) be represented by  $\text{Eu}^{2+}\text{Co}^{2+}\text{Co}^{2+}\text{P}^{3-}\text{P}^{3-}$  (31). In  $\text{EuNi}_2\text{P}_2$  the short P-P distance of 2.37  $\text{\AA}$  comes close to the typical two-electron bond distance of 2.21  $\text{\AA}$  (see for instance references 33, 40-

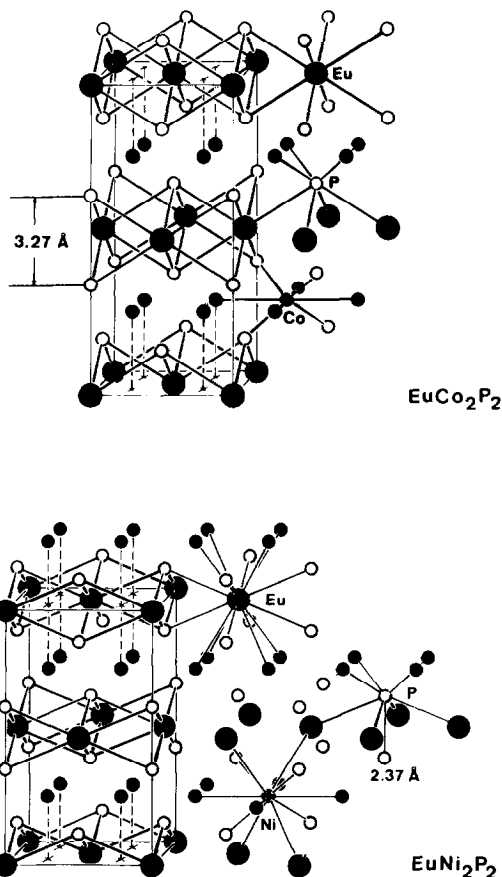


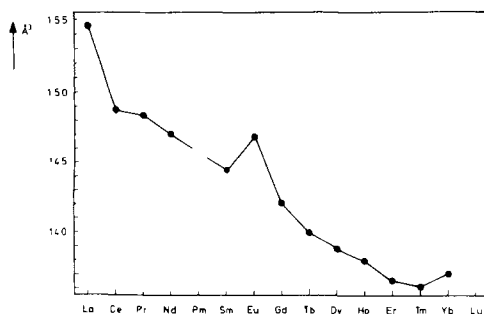
FIG. 1. Crystal structures and near-neighbor environments of  $\text{EuNi}_2\text{P}_2$  and  $\text{EuCo}_2\text{P}_2$ . The outlined all-face-centered cells have double the volumes of the conventional body-centered cells.

43). Thus, to a first approximation, the P atoms may be considered as forming pairs, which according to Zintl's concept (44) results in the formal oxidation number  $-2$  for the P atoms. Since the cell volume of  $\text{EuNi}_2\text{P}_2$  exceeds its interpolated volume on the plot for the  $\text{LnNi}_2\text{P}_2$  series (Fig. 2), Eu might be assumed divalent, and the compound could to a first approximation be rationalized with the formula  $\text{Eu}^{2+}\text{Ni}^{1+}\text{Ni}^{1+}[\text{P}_2]^{4-}$ . On closer inspection of the cell volumes of related compounds, however, an intermediate (nonintegral) valence is suggested for at least the Eu atoms in  $\text{EuNi}_2\text{P}_2$ .

TABLE IV  
 STRUCTURE FACTORS FOR  $\text{EuNi}_2\text{P}_2$ 

HKL	FD	FC	HKL	FD	FC	HKL	L	FD	FC
1 1 0	56	56	1 6 3	42	42	1 1	8	44	42
0 2 0	117	119	0 0 4	105	107	0 2	8	118	115
2 2 0	119	133	1 1 4	23	-16	2 2	8	103	104
1 3 0	44	44	0 2 4	104	102	1 3	8	38	36
3 3 0	38	38	2 2 4	88	89	3 3	8	32	31
0 4 0	96	112	1 3 4	11	-6	0 4	6	87	85
2 4 0	92	101	3 3 4	8	-3	2 4	8	78	77
4 4 0	70	75	0 4 4	69	70	1 5	8	24	26
1 5 0	32	33	2 4 4	60	63	0 1	9	46	45
3 5 0	28	27	4 4 4	45	48	1 2	9	43	41
0 6 0	65	69	1 5 4	5	3	0 3	9	39	37
2 6 0	60	63	3 5 4	8	4	2 3	9	35	34
0 1 1	69	68	0 6 4	38	45	1 4	9	33	32
1 2 1	61	61	0 1 5	102	97	3 4	9	28	27
0 3 1	53	53	1 2 5	87	87	0 5	9	27	27
2 3 1	46	47	0 3 5	78	77	0 0 10		18	18
1 4 1	41	42	2 3 5	70	70	1 1 10		91	86
3 4 1	34	35	1 4 5	62	63	0 2 10		17	17
0 5 1	34	35	3 4 5	51	52	2 2 10		18	17
2 5 1	30	33	0 5 5	54	52	1 3 10		74	70
1 6 1	26	28	2 5 5	48	47	3 3 10		60	59
0 0 2	14	17	0 0 6	19	18	0 4 10		16	15
1 1 2	120	108	1 1 6	118	117	2 4 10		14	14
0 2 2	18	18	0 2 6	19	19	0 1 11		66	62
2 2 2	18	18	2 2 6	16	19	1 2 11		61	56
1 3 2	99	110	1 3 6	93	94	0 3 11		55	51
3 3 2	81	88	3 3 6	74	76	2 3 11		50	47
0 4 2	19	18	0 4 6	17	18	1 4 11		46	43
2 4 2	18	18	2 4 6	16	17	0 0 12		62	60
4 4 2	13	16	4 4 6	15	15	1 1 12		4	3
1 5 2	67	71	1 5 6	62	63	0 2 12		61	54
3 5 2	57	60	3 5 6	52	53	2 2 12		53	50
0 6 2	16	15	0 1 7	58	52	1 3 12		7	4
0 1 3	108	102	1 2 7	48	46	0 1 13		58	50
1 2 3	90	95	0 3 7	44	42	1 2 13		51	46
0 3 3	82	84	2 3 7	39	38	0 3 13		47	42
2 3 3	72	75	1 4 7	35	35	0 0 14		12	16
1 4 3	66	68	3 4 7	31	30	1 1 14		64	58
3 4 3	53	55	0 5 7	30	30	0 2 14		15	15
0 5 3	54	55	2 5 7	28	28	0 1 15		28	27
2 5 3	49	50	0 0 8	127	126				

An intermediate valence for Eu in a  $\text{ThCr}_2\text{Si}_2$ -type compound was first concluded from Mössbauer data for  $\text{EuCu}_2\text{Si}_2$  (45) and confirmed by an X-ray photoemission study (46). In that compound the  $^{151}\text{Eu}$  isomer shift changes continuously with temperature. It corresponds to  $\text{Eu}^{3+}$  at 4 K, and at 670 K it indicates an about equal population of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ . In  $\text{EuFe}_2\text{Si}_2$ ,  $\text{EuCo}_2\text{Si}_2$ , and  $\text{EuNi}_2\text{Si}_2$  two  $^{151}\text{Eu}$  Mössbauer signals are observed corresponding to the two valence states of Eu. The relative amounts are different in the three compounds (21). Their cell volumes also reflect their intermediate valence character. These values are only between 0.2 and 4.1 Å<sup>3</sup>


 FIG. 2. Cell volumes of  $\text{LnNi}_2\text{P}_2$  compounds with  $\text{ThCr}_2\text{Si}_2$ -type structure vs the atomic number of the rare earth elements.

higher than the cell volumes interpolated for them from the corresponding Sm and Gd compounds (3, 5, 11, 22), where the rare earth elements are trivalent. In contrast the cell volumes of  $\text{EuAg}_2\text{Si}_2$  (5),  $\text{EuNi}_2\text{Ge}_2$  (2), and  $\text{EuCu}_2\text{Ge}_2$  (21) where Eu is divalent (21) exceed the value interpolated from the Sm and Gd compounds (3, 5, 25) by between 9.6 and 11.1 Å<sup>3</sup>. Since the cell volume of  $\text{EuNi}_2\text{P}_2$  is only 3.6 Å<sup>3</sup> larger than the value interpolated from  $\text{SmNi}_2\text{P}_2$  and  $\text{GdNi}_2\text{P}_2$ , it seems likely that some Eu is trivalent in  $\text{EuNi}_2\text{P}_2$ .

This is also supported by a comparison of the near-neighbor environments in  $\text{EuCo}_2\text{P}_2$  and  $\text{EuNi}_2\text{P}_2$ . In both compounds the Eu

 TABLE V  
 INTERATOMIC DISTANCES AND SELECTED INTERATOMIC ANGLES OF  $\text{EuNi}_2\text{P}_2$  AS COMPARED TO THE CORRESPONDING VALUES OF  $\text{EuCo}_2\text{P}_2$  (GIVEN IN PARENTHESES)<sup>a</sup>

Eu: 8 P	3.026 (3.125)	P-Ni-P (4×)	105.4 (106.8)
8 Ni	3.079 (3.404)	P-Ni-P (2×)	118.1 (115.0)
Ni: 4 P	2.296 (2.233)	Ni-P-Ni (4×)	74.6 ( 73.2)
4 Ni	2.785 (2.662)	Ni-P-Ni (2×)	118.1 (115.0)
4 Eu	3.079 (3.404)	Ni-P-P (4×)	121.0 (122.5)
P: 4 Ni	2.296 (2.233)	Eu-P-Eu (4×)	81.2 ( 74.1)
1 P	2.371 (3.272)	Eu-P-Eu (2×)	133.9 (116.9)
4 Eu	3.026 (3.125)		

<sup>a</sup> All distances shorter than 3.5 Å are listed. Standard deviations are all less than 0.005 Å and 0.1°, respectively.

atoms are surrounded by 8 P and 8 T (Co, Ni) atoms. The interatomic distances of Eu to its neighbors in  $\text{EuCo}_2\text{P}_2$  are considerably larger than the corresponding distances in the Ni compounds (Table V). Thus the valency of Eu in  $\text{EuNi}_2\text{P}_2$  must be higher than its valency in  $\text{EuCo}_2\text{P}_2$ . In the latter compound Eu probably is divalent or very close to that; however, since the corresponding Sm and Gd cobalt phosphides are not known, no conclusions can be drawn from a comparison of cell volumes.

The near-neighbor environments of the Ni atoms in  $\text{EuNi}_2\text{P}_2$  also show some differences to the environments of the Co atoms in  $\text{EuCo}_2\text{P}_2$ . In both compounds the T atoms are approximately tetrahedrally coordinated by P atoms. It was expected (31) that the great difference in the  $c/a$  ratios (this ratio is 3.01 for  $\text{EuCo}_2\text{P}_2$  and 2.40 for  $\text{EuNi}_2\text{P}_2$ ) was due to the tendency of  $\text{Ni}^{2+}$  for square-planar coordination. However, as was discussed above, these differences are due to the entirely different bonding situation of the P atoms, which results in an oxidation number of less than +2 (possibly as low as +1) for Ni. Some Ni-Eu bonding may be present: the Eu-Ni distances of 3.08 Å are close to 3.05 Å, which is the sum of the metallic radii for coordination number 12 assuming trivalent Eu (47, 48).

Another interesting point is the cell volume of  $\text{YNi}_2\text{P}_2$ . It fits between the volumes of  $\text{TbNi}_2\text{P}_2$  and  $\text{DyNi}_2\text{P}_2$ . This is analogous to the situation in the corresponding  $\text{LnNi}_2\text{Si}_2$  compounds (2, 49) and other more or less "intermetallic," isotypic series of compounds, as for instance in the  $\text{Ln}_3\text{Rh}_2$  compounds with  $\text{Y}_3\text{Rh}_2$ -type structure (50) or in the  $\text{LnNi}_3$  compounds with  $\text{PuNi}_3$ -type structure (51). In the series  $\text{Ln}_2\text{Ni}_7$  (51) and  $\text{Ln}_2\text{Ni}_{12}\text{P}_7$  (36) the cell volume of the Y compounds is relatively slightly larger and fits between the corresponding Gd and Tb compounds. In ionic compounds, however, the size of Y is relatively smaller. For fluorides and oxides the

radii of  $\text{Y}^{3+}$  fit between the radii of  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  for the coordination number 6 and between  $\text{Dy}^{3+}$  and  $\text{Ho}^{3+}$  for the coordination numbers 8 and 9 (52).

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