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Structural Investigations of Ternary Lanthanoid and Uranium Nickel Phosphides

W. K. HOFMANN AND W. JEITSCHKO*

Abteilung Chemie, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50, West Germany

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The new compound $LaNi_5P_3$ was prepared by reaction of the elemental components in a tin flux. It crystallizes with the orthorhombic $LaCo_5P_3$-type structure, space group *Cmcm*, and the lattice constants $a = 3.642(1)$, $b = 11.716(2)$, $c = 11.494(3)$. Its structure was refined from single-crystal X-ray data to $R = 0.070$ (759 *F* values, 16 variables). UNi_2P_2 with $ThCr_2Si_2$-type structure was prepared for the first time. The crystal structures of the $ThCr_2Si_2$-type compounds $LaNi_2P_2$ ($R = 0.016$, 190 *F*'s, 11 variables) and $CeNi_2P_2$ ($R = 0.015$, 199 *F*'s, 11 variables) were refined from single-crystal X-ray data. Chemical bonding in the $ThCr_2Si_2$-type compounds is discussed.

Introduction

Lanthanoid (*Ln*) nickel phosphides with $ThCr_2Si_2$-type structure have been known for some time (*1, 2*). A structure refinement from single-crystal X-ray data was carried out for $EuNi_2P_2$ (*2*). In this compound Eu is at least partially divalent. In the corresponding La and Ce compounds the plot of the cell volumes (Fig. 1) suggests the usual trivalency for La while Ce in $CeNi_2P_2$ seems to be at least partially tetravalent. To obtain a better understanding of chemical bonding in these compounds we have now refined the crystal structures of $LaNi_2P_2$ and $CeNi_2P_2$. The refinement of the Ce compound is of special interest when compared to that of the Eu compound, because the cell volumes of the two compounds are almost equal, although the valences of their *Ln* components differ. The structures of the new related compounds $LaNi_5P_3$ and UNi_2P_2 are also reported.

Syntheses

Starting materials were ingots of the lanthanoids and powders of uranium, nickel, and red phosphorus, all with stated purities of 99.9% or better. Filings of the ingots were prepared under dried paraffin oil, adhering iron particles were removed with a magnet, and the paraffin oil was washed out with petrol ether. The dry powders were not allowed to contact air prior to sealing under vacuum for the syntheses.

Small single crystals of $LaNi_2P_2$ and $CeNi_2P_2$ were grown from a tin flux. Stoichiometric mixtures of the elemental components together with about 25 to 75 at.% tin (purity 99.9%) were sealed in evacuated silica tubes, annealed at 900°C for about 5

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* New address: Anorganisch-Chemisches Institut, Westfälische Wilhelms-Universität, D-4400 Münster, West Germany.

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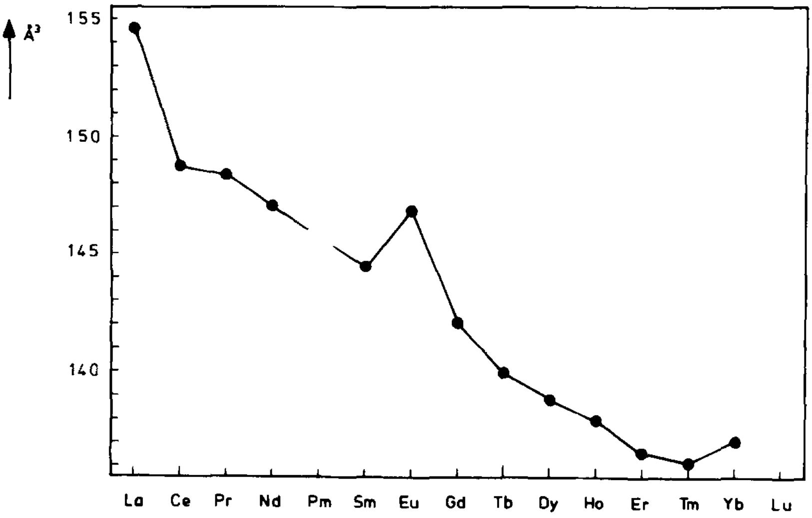

FIG. 1. Cell volumes of $LnNi_2P_2$ compounds with $ThCr_2Si_2$-type structure.

days, and slowly cooled to room temperature within 1 or 2 days. The tin-rich matrix was dissolved with moderately dilute hydrochloric acid (1 : 1) which left the crystals of the ternary compounds essentially unattacked.

Single crystals of $LaNi_5P_3$ were also prepared this way by annealing the powders in the atomic ratios La : Ni : P : Sn = 5 : 45 : 25 : 25. This compound was also obtained in pure form by reaction of the stoichiometric mixture of the elements in evacuated silica tubes by adding about 1 at.% iodine as a mineralizer. The sample was annealed for 10 days at 700°C, cold-pressed, again annealed at 700°C for 10 days, and quenched to room temperature. The new compound UNi_2P_2 was prepared by sintering the elemental components in evacuated silica tubes for 5 days at 800°C.

Energy dispersive fluorescence analyses of crystals of $LaNi_2P_2$, $CeNi_2P_2$, and $LaNi_5P_3$ in a scanning electron microscope showed their tin content to be less than 0.3 at.%. Silicon (from the silica tubes through reduction by the lanthanoid component) is more difficult to determine this way because of the vicinity of its fluorescence peak to that of phosphorus. The spectra gave a slight indication for silicon in $LaNi_2P_2$ and $CeNi_2P_2$; it was, however, certainly less than 4 at.% in both compounds.

Lattice Constants

X-Ray powder patterns of the products were recorded with monochromated $CuK\alpha_1$ radiation in a Guinier- de Wolff camera with α-quartz ($a = 4.9130$, $c = 5.5046$ Å) as standard. The patterns of $LaNi_2P_2$, $CeNi_2P_2$, and UNi_2P_2 were readily indexed on the basis of the body-centered tetragonal cell typical for $ThCr_2Si_2$-type compounds. The lattice constants (Table I) were refined by a least-squares treatment of the data. Table II shows as an example the evaluation of the powder pattern of UNi_2P_2. The pattern of $LaNi_5P_3$ was indexed and the lattice constants were refined only after the structure was determined from the single-crystal X-ray data.

Structure Refinements

Single crystals of $LaNi_2P_2$, $CeNi_2P_2$, and $LaNi_5P_3$ were examined on a Buerger pre-

TABLE I

LATTICE CONSTANTS OF $LaCo_5P_3$- AND $ThCr_2Si_2$-TYPE COMPOUNDS[a]

Compound	System	a (Å)	b (Å)	c (Å)	c/a	V (Å^3)	Ref.
$LaNi_5P_3$	Orthorhombic	3.642(1)	11.716(2)	11.494(3)		490.5	[b]
$LaCo_5P_3$	Orthorhombic	3.651(1)	11.573(2)	11.459(2)		484.2	3
$LaNi_2P_2$	Tetragonal	4.010(1)		9.604(2)	2.395	154.5	[b]
$LaNi_2P_2$	Tetragonal	4.007(2)		9.632(6)	2.404	154.6	2
$CeNi_2P_2$	Tetragonal	3.958(1)		9.489(2)	2.397	148.7	[b]
$CeNi_2P_2$	Tetragonal	3.955(2)		9.505(6)	2.403	148.7	2
UNi_2P_2	Tetragonal	3.885(1)		9.404(3)	2.421	141.9	[b]

[a] Standard deviations in the least significant digits (in all tables) are given in parentheses.
[b] This work.

cession camera. The diffraction patterns of $LaNi_2P_2$ and $CeNi_2P_2$ had the Laue symmetry *4/mmm* and body-centered extinctions. The structure refinements gave no indication for a symmetry lower than *I4/mmm*. The diffraction patterns of $LaNi_5P_3$ had the Laue symmetry *mmm* and were fully compatible with the space group *Cmcm* established during the structure refinements.

TABLE II

POWDER PATTERN OF UNi_2P_2 WITH $ThCr_2Si_2$-TYPE STRUCTURE[a]

hkl	Q_o	Q_c	I_o	I_c
002	455	452	m	126
101	776	776	vs	784
110	1324	1325	s	192
103	1679	1680	vs	681
112	1780	1777	vs	1000
004	1810	1809	m	161
200	2650	2650	s	384
202	3101	3103	w	51
114	—	3135	—	14
211	3426	3426	s	213
105	3493	3490	s	225
006	—	4071	—	9
213	4336	4331	s	319
204	4464	4460	m	153
220	5301	5300	m	120
116	5395	5396	m	166
222	—	5753	—	23

[a] For the calculation of the pattern (*4*) the parameter of the P atoms was assumed as obtained in the structure refinement of $CeNi_2P_2$. The Q values are defined by $Q = 1000/d^2$ (Å^{-2}).

Single-crystal intensity data for the three compounds were collected in an automated four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation, a scintillation counter, and a pulse height discriminator. Background counts were taken at both ends of the θ–2θ scans and an empirical absorption correction was applied from psi scan data. Additional information on the data collection is summarized in Table III.

The structure of $LaNi_5P_3$ was determined from Patterson and difference Fourier syntheses. Later $LaNi_5P_3$ was recognized to be isotypic with $LaCo_5P_3$ (*3*). Starting parame-

TABLE III

CRYSTAL DATA AND SOME RESULTS OF THE STRUCTURE REFINEMENTS OF $LaNi_5P_3$, $LaNi_2P_2$, AND $CeNi_2P_2$

Compound	$LaNi_5P_3$	$LaNi_2P_2$	$CeNi_2P_2$
Structure type	$LaCo_5P_3$	$ThCr_2Si_2$	$ThCr_2Si_2$
Formula units/cell	$Z = 4$	$Z = 2$	$Z = 2$
Portion of reciprocal space measured	$\frac{1}{4}$	All	All
Up to 2θ	90°	90°	90°
Intensity data collected	2586	3038	2942
Internal R (on F's)	0.039	0.033	0.028
Ratio of highest to lowest transmission	2.34	1.17	1.70
Final conventional residual	$R = 0.070$	$R = 0.016$	$R = 0.015$
For unique F values $>2\sigma$	759	190	199
Number of variable parameters	16	11	11

TABLE IV

ATOMIC PARAMETERS OF $LaNi_5P_3$

	Cmcm	*x*	*y*	*z*	*B* (Å^2)
La	4*c*	0	0.3370(1)	$\frac{1}{4}$	0.28(1)
Ni(1)	4*b*	0	$\frac{1}{2}$	0	0.30(3)
Ni(2)	8*f*	0	0.0510(2)	0.1453(2)	0.34(2)
Ni(3)	8*f*	0	0.3018(2)	0.5677(2)	0.36(2)
P(1)	8*f*	0	0.1181(3)	0.5399(3)	0.22(4)
P(2)	4*c*	0	0.6162(5)	$\frac{1}{4}$	0.32(6)

ters for the refinements of $LaNi_2P_2$ and $CeNi_2P_2$ were taken from $EuNi_2P_2$ (*2*). The three structures were refined by full matrix least-squares cycles with scattering factors for neutral atoms (*5*), corrected for anomalous dispersion (*6*). Unit weights were used. Isotropic factors accounting for secondary extinction were refined as least-squares parameters. To check for possible deviations from full occupancy of the atomic positions we have also refined occupancy parameters. No significant deviations from full occupancy were obtained for the structure of $LaNi_5P_3$. However, for $LaNi_2P_2$ and $CeNi_2P_2$ we obtained slight (albeit statistically significant) deviations from full occupancy for the Ni and P positions.

Final residuals are listed in Table III, positional parameters in Tables IV and V, and interatomic distances in Tables VI and VII. Listings of structure factors can be obtained from the authors.

Discussion

The structure refinements of $LaNi_2P_2$ and $CeNi_2P_2$ resulted in unusually low *R* values. This is because absorption effects were greatly reduced by averaging, in general, 16 equivalent observations for every unique structure amplitude. Thus the small deviations (about 5%) from full occupancy of the Ni and P positions are highly significant from the standpoint of error analysis. It is, however, difficult to assess the physical meaning of this result. It could be that there

TABLE V

ATOMIC PARAMETERS OF $LaNi_2P_2$ AND $CeNi_2P_2$[a]

	I4/mmm	Occupancy	*x*	*y*	*z*	$U_{11} = U_{22}$	U_{33}	B_{equ}
$LaNi_2P_2$								
La	2a	1	0	0	0	0.0046(1)	0.0058(1)	0.396(3)
Ni	4d	0.942(3)	0	$\frac{1}{2}$	$\frac{1}{4}$	0.0089(2)	0.0065(2)	0.639(6)
P	4e	0.951(6)	0	0	0.3700(2)	0.0055(3)	0.0064(4)	0.46(1)
$CeNi_2P_2$								
Ce	2a	1	0	0	0	0.0044(1)	0.0039(1)	0.337(3)
Ni	4d	0.949(3)	0	$\frac{1}{2}$	$\frac{1}{4}$	0.0096(2)	0.0071(2)	0.694(6)
P	4e	0.957(5)	0	0	0.3733(2)	0.0066(3)	0.0057(4)	0.50(1)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots]$. In this structure type the thermal parameters U_{12}, U_{13}, and U_{23} are equal to zero for all atoms. The last column contains the equivalent isotropic thermal parameter *B* (Å^2).

TABLE VI

INTERATOMIC DISTANCES IN $LaNi_5P_3$[a]

La:	4 P(1)	3.071	Ni(3):	1 P(1)	2.175
	2 P(2)	3.164		1 P(2)	2.305
	1 P(2)	3.270		2 P(1)	2.392
	4 Ni(3)	3.217		1 Ni(1)	2.449
	4 Ni(2)	3.324		2 Ni(2)	2.662
	2 Ni(1)	3.449		2 Ni(3)	2.686
	2 Ni(2)	3.561		2 La	3.217
	2 Ni(3)	3.676		1 La	3.676
	2 La	3.642			
			P(1):	1 Ni(3)	2.175
Ni(1):	4 P(1)	2.332		1 Ni(2)	2.267
	2 Ni(3)	2.449		1 Ni(2)	2.323
	4 Ni(2)	2.543		2 Ni(1)	2.332
	2 La	3.449		2 Ni(3)	2.392
				2 La	3.071
Ni(2):	1 P(1)	2.267			
	2 P(2)	2.312	P(2):	2 Ni(3)	2.305
	1 P(1)	2.323		4 Ni(2)	2.312
	1 Ni(2)	2.406		2 La	3.164
	2 Ni(1)	2.543		1 La	3.270
	2 Ni(3)	2.662			
	2 La	3.324			
	1 La	3.561			

[a] For the La atoms all distances shorter than 3.7 Å are given. The shortest not listed Ni–Ni and Ni–P interactions are greater than 3.15 Å. The shortest nonbonding P–P distance is 2.914 Å. Standard deviations are all less than or equal to 0.004 Å.

are indeed some Ni and P positions unoccupied. The lack in the scattering power of the Ni positions could also be accounted for by a partial occupancy of these sites (about 12%) by P atoms. In the closely related $CaBe_2Ge_2$-type structure (*7*) which occurs for the related compositions $LaNi_2Sb_2$ and $CeNi_2Sb_2$ and the corresponding bismuthides (*8*), 50% of the Ni positions are occupied by the metalloid atoms. This shows that the Ni site is well suited for the metalloid atoms. On the other hand, the structures of $LaNi_2P_2$ and $CeNi_2P_2$ cannot be considered as transitional from the $ThCr_2Si_2$ type to the $CaBe_2Ge_2$ type, because in $LaNi_2Sb_2$ (and the other related $CaBe_2Ge_2$-type compounds) 50% of the metalloid positions are occupied by Ni atoms. This would have caused the scattering power of the P positions in $LaNi_2P_2$ and $CeNi_2P_2$ to increase rather than decrease. We have also considered that Si impurity atoms could occupy the P positions; however, about 70% of the P positions would need to be occupied by Si atoms to account fully for this loss in scattering power. Such a high Si content can certainly be ruled out on the basis of the energy dispersive analysis mentioned above, although *some* silicon may be present on these sites. Systematic errors in the data sets or in the calculated atomic scattering factors were also considered, but seem less likely to us. Because of the difficulty in assessing the true causes for the slightly smaller scattering powers of the Ni and P positions we maintain the ideal formulas $LaNi_2P_2$ and $CeNi_2P_2$. These ideal compositions may after all well be within the homogeneity ranges of the compounds. For the purpose of the following discussion we want to recall that the isotypic compound $EuNi_2P_2$ (*2*) was prepared in the same way and therefore impurity levels should be similar in the three compounds.

TABLE VII

INTERATOMIC DISTANCES IN $LnNi_2P_2$ (Ln = La, Ce, Eu) COMPOUNDS WITH $ThCr_2Si_2$ STRUCTURE[a]

	$LaNi_2P_2$	$CeNi_2P_2$	$EuNi_2P_2$[b]	Ce/Eu ratio[c]
Ln: 8 P	3.099	3.046	3.026	1.007
8 Ni	3.128	3.089	3.079	1.003
Ni: 4 P	2.312	2.299	2.296	1.001
4 Ni	2.836	2.799	2.785	1.005
4 Ln	3.128	3.089	3.079	1.003
P: 4 Ni	2.312	2.299	2.296	1.001
1 P	2.497	2.405	2.371	1.014
4 La	3.099	3.046	3.026	1.007

[a] All distances shorter than 3.5 Å are listed. Standard deviations are all less than 0.003 Å.

[b] From Ref. (*2*).

[c] The last column lists the ratio of the bond lengths of the Ce and Eu compound.

Chemical bonding in $EuNi_2P_2$ was to a first approximation rationalized with the formula $Eu^{2+}Ni^{1+}Ni^{1+}[P_2]^{4-}$ where the superscripts represent oxidation numbers of the metal atoms with respect to the (more electronegative) P atoms (*2*). These oxidation numbers should not be mistaken for ionic charges, which certainly will be small because of the essentially covalent character of the metal–phosphorus interactions. In deriving this formula it is assumed that the P atoms form single-bonded pairs. In addition to these interactions considerable Ni–Ni bonding can be concluded from the short Ni–Ni distances, and some Eu–Ni bonding also seems probable. In further fine tuning of this bonding description it was concluded from a comparison of cell volumes that Eu in $EuNi_2P_2$ has most likely a mixed or intermediate (between 2 and 3) valence (*2*). This was confirmed by Mössbauer and X-ray absorption edge measurements (*9*).

The P–P distance of 2.37 Å in $EuNi_2P_2$ is longer than the typical single bond distance of 2.21 Å. The question arises: why? An answer to this can be given by a comparison of the bond lengths of $EuNi_2P_2$ and $CeNi_2P_2$. Both compounds have nearly the same lattice constants, but the Ce compound provides about one more valence electron per formula unit to the structure (the valency of Eu in this compound is intermediate between 2 and 3, that of Ce is between 3 and 4; both are estimates from the cell volumes). A look at Table VII shows that corresponding to the slightly larger lattice constants of the Ce compound all distances are slightly larger in the Ce compound than in the Eu compound. However, the greatest difference (as judged from the bond length ratios) occurs for the P–P bond. Since it is stretched even further by the additional valence electron of the Ce compound, one can conclude that the additional valence electron per formula unit is accommodated in an antibonding P–P level. In other words the P–P bonding levels are all filled in the Eu compound and the unusual length of the P–P bond in that compound is due to partial filling of antibonding P–P levels which are further filled in the Ce compound.

The Ni–P bonds are least affected by the additional valence electron of $CeNi_2P_2$. This may be taken as an indication for the Ni–P bonding band being below the Fermi surface in both compounds. The Ni–P bond lengths of nearly 2.30 Å in both compounds, however, are greater than the two-electron bond lengths of 2.21 Å in NiP_2 (*10*) and $Ce_6Ni_6P_{17}$ (*11*). This can be rationalized by the higher coordination number of the Ni atoms in the $LnNi_2P_2$ compounds: In NiP_2 and $Ce_6Ni_6P_{17}$ the Ni atoms have approximately square planar coordination; in the $LnNi_2P_2$ compounds the coordination is a distorted tetrahedron of P atoms augmented by four Ni atoms (at about 2.8 Å) which are in a square which is perpendicular to the $\bar{4}$ axis of the P tetrahedron (Fig. 2). This coordination implies that the tetrahedral Ni–P bonds are essentially formed by the sp^3 hybrid of the Ni atoms while the four bonds (of bond order $\frac{1}{4}$ each) to the Ni atoms involve the remaining half-occupied *d* orbital.

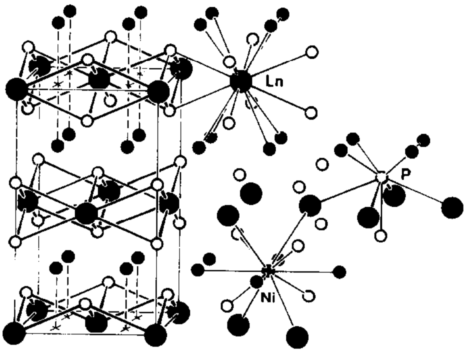

FIG. 2. Crystal structure and near neighbor environments in $LnNi_2P_2$ compounds with $ThCr_2Si_2$-type structure. The outlined face-centered cell has an *a* translation period which is $\sqrt{2}$ times larger than the conventional body-centered cell.

The P atoms have, besides the one P neighbor, four Ni neighbors which, together with the P neighbor, form a square pyramid. Considering the tendency of transition metal polyphosphides to form two-electron bonds (*12*) one could suppose that the P atoms are sp^3d hybridized. Such sp^3d hybrids were suggested for P atoms in MoP_2 and β-WP_2 in agreement with the diamagnetism and semimetallic character of the electrical conductivity of both compounds (*13*). However, in the $Ln$$Ni_2P_2$ compounds the involvement of the P d orbitals is difficult to assess from near neighbor environments alone because, as already mentioned above, here the Ni–P bonds are longer than typical two-electron bonds.

The structure of $LaNi_5P_3$ has higher coordination numbers for all atoms; thus counting two valence electrons for each short near neighbor interaction would not provide a good starting point for a discussion of the bonding situation. This structure is similar, in both composition and near neighbor environments, to the $Zr_2Fe_{12}P_7$-type structure which was found in all *Ln*–Ni–P systems except the La–Ni–P system (*14*). Both structures can be classified topologically as belonging to a large family of structures with a trigonal prismatic environment of the metalloid atoms (*15*).

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