Inorg. Chem. **1998,** *37,* 5431−5438

Lanthanum Nickel Silicides with the General Formula $La_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$ and Other Series of Hexagonal Structures with Metal:Metalloid Ratios Close to 2:1

Yurij M. Prots' and Wolfgang Jeitschko*

Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8,
D-48149 Münster, Germany

Received April 7, 1998

The closely related crystal structures of the compounds $La_6Ni_2Si_3$ ($La_{12}Ni_4Si_6$, $n = 2$) and $La_5Ni_2Si_3$ ($La_{20}Ni_8Si_{12}$, $n = 3$) as well as those of the new compounds $La_{15}Ni_7Si_{10}$ ($La_{30}Ni_{14}Si_{20}$, $n = 4$) and $La_{21}Ni_{11}Si_{15}$ ($La_{42}Ni_{22}Si_{30}$, $n = 5$) were determined from single-crystal X-ray diffractometer data. In these hexagonal silicides (space group $P6_3/m$) almost all atoms are situated on mirror planes, which extend perpendicular to the short c axes. The only exceptions are nickel atoms located on the 6_3 axes, which show some disorder resulting in the exact compositions $La_6Ni_{1.54(2)}Si_3$ [$a = 1224.3(1)$ pm, $c = 438.3(1)$ pm, $Z = 2$, $Ce_6Ni_2Si_3$ type structure], $La_5Ni_{1.75(1)}Si_3$ [$a = 1624.4(3)$ pm, $c = 434.2(2)$ pm, $Z = 4$, $Ce_5Ni_2Si_3$ type], $La_{15}Ni_{6.62(2)}Si_{10}$ [$a = 2021.2(3)$ pm, $c = 435.1(1)$ pm, $Z = 2$, $Pr_{15}Ni_7Si_{10}$ type], and $La_{21}Ni_{10.49(3)}Si_{15}$ [$a = 2427.7(3)$ pm, $c = 435.2(1)$ pm, $Z = 2$, a new structure type]. All of these structures have building elements which resemble the AlB_2 type structure. In these the lanthanum atoms correspond to the aluminum atoms of AlB_2, while the nickel and silicon atoms occupy the boron positions in an ordered manner. Other series of ternary hexagonal lanthanoid and actinoid transition metal silicides and phosphides, e.g., the series with the general formula $R_{n(n-1)}Ni_{(n+1)(n+2)}P_{n(n+1)+1}$ ($R =$ Th, U), are briefly reviewed, and the systematics in the space groups and the diffraction patterns of these compounds are pointed out.

Introduction

More than 20 years ago a series of related cerium nickel silicides "Ce_2NiSi", "$Ce_{15}Ni_4Si_{13}$", and $Ce_6Ni_2Si_3$ were synthesized by Bodak and Gladyshevskii.[1−3] The general formula for these compounds was given as $Ce_{n^2+3n+2}(Ni, Si)_{2n^2+2}$, since at that time—when structures were determined from film data—it was generally believed that nickel and silicon can substitute for each other in such compounds. Later, when the crystal structures of such compounds were determined from diffractometer data, it was recognized that frequently the late transition metal and the silicon atoms order. Hovestreydt and Parthé[4] reported the compound $Pr_{15}Ni_7Si_{10}$ with an ordered distribution of the nickel and silicon atoms, and they suggested "$Ce_{15}Ni_4Si_{13}$" to be isotypic with $Pr_{15}Ni_7Si_{10}$. They also gave a formula for this series of compounds accounting for the ordered distribution of the nickel and silicon atoms, which corresponds to the formula $R_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$ used in the present paper. We report on four compounds of this series of structures with lanthanum as the rare earth metal component with $n = 2$, 3, 4, and 5. For the previously published compounds "La_2NiSi"[1] and $La_6Ni_2Si_3$[3] we verify that the nickel and silicon atoms are ordered. The ideal formula for "La_2NiSi" is $La_5Ni_2Si_3$ ($n = 3$), whereas the formula $La_6Ni_2Si_3$ ($n = 2$) remains correct. The other two compounds $La_{15}Ni_7Si_{10}$ ($n = 4$) and $La_{21}Ni_{11}Si_{15}$ ($n = 5$) are new. The latter crystallizes with a new structure type. A preliminary account of this work was presented at a conference.[5]

Preparation, Lattice Constants, and Properties

All compounds were prepared by reaction of the elemental components (lanthanum ingots, nominal purity 99.9%; nickel powder, 150 mesh, 99.9%, pressed to pellets; silicon pieces, 6N) in an arc-melting furnace under an argon atmosphere. The samples were turned over and remelted twice to enhance their homogeneity. They were then sealed in evacuated silica tubes, annealed for 2 weeks at 800 °C, and quenched in water.

The Guinier powder diagrams of the samples were compared to those calculated[6] for possible structure types with related compositions. This way it was recognized that the compounds $La_6Ni_{2-x}Si_3$, $La_5Ni_{2-x}Si_3$, and $La_{15}Ni_{7-x}Si_{10}$ were isotypic with the structures first described for $Ce_6Ni_2Si_3$,[3] "Ce_2NiSi",[1] and $Pr_{15}Ni_7Si_{10}$.[4] Knowing the ideal compositions from the structure determinations, we could prepare the compounds in nearly pure form by reaction of stoichiometric amounts of the elemental components. After we recognized that these compounds form a homologous series, a model for the structure of $La_{21}Ni_{11}Si_{15}$ was extrapolated, and single crystals of this predicted compound could be isolated from a sample with the ideal composition.

The lattice constants of these four compounds (Table 1) were obtained by least-squares fits of the Guinier powder data recorded at room temperature with Cu Kα radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard.

---

(1) Bodak, O. I.; Gladyshevskii, E. I.; Mys'kiv, M. G. *Sov. Phys. Crystallogr.* **1972**, *17*, 439.
(2) Mys'kiv, M. G.; Bodak, O. I.; Gladyshevskii, E. I. *Sov. Phys. Crystallogr.* **1974**, *18*, 450.
(3) Bodak, O. I.; Gladyshevskii, E. I.; Kharchenko, O. I. *Sov. Phys. Crystallogr.* **1974**, *19*, 45.
(4) Hovestreydt, E.; Parthé, E. *Acta Crystallogr.* **1985**, *C41*, 310.
(5) Prots', Yu. M.; Jeitschko, W. *Z. Kristallogr. Suppl.* **1997**, *12*, 137.
(6) Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* **1977**, *10*, 73.
(7) Parthé, E.; Gelato, L.; Chabot, B.; Penzo, M.; Cenzual, K.; Gladyshevskii, R. TYPIX, Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types. In *Gmelin Handbook of Inorganic and Organometallic Chemistry*; Springer: Berlin, 1994; Vols. 1−4.

10.1021/ic980397w CCC: $15.00

Table 1. Crystal Data for $La_6Ni_{2-x}Si_3$, $La_5Ni_{2-x}Si_3$, $La_{15}Ni_{7-x}Si_{10}$, and $La_{21}Ni_{11-x}Si_{15}$[a]

composition	$La_6Ni_{1.54(1)}Si_3$	$La_5Ni_{1.75(1)}Si_3$	$La_{15}Ni_{6.62(2)}Si_{10}$	$La_{21}Ni_{10.49(3)}Si_{15}$
lattice constants[b]				
a (pm)	1224.3(1)	1624.4(3)	2021.2(3)	2427.7(3)
c (pm)	438.3(1)	434.4(2)	435.1(1)	435.2(1)
V (nm^3)	0.5690(1)	0.9927(5)	1.5394(4)	2.2213(6)
formula units/cell, *Z*[c]	2	4	2	2
formula mass	1008.1	881.55	2753.2	3954.3
space group	$P6_3/m$ (No. 176) for all four compounds			
temp (°C)	22	22	22	22
wavelength λ (pm)	710.69	710.69	710.69	710.69
ρ_{calcd} (g cm^{-3})	5.88	5.90	5.94	5.91
μ (mm^{-1}, Mo Kα)	24.74	24.55	24.60	24.40
R (F_o)	0.029	0.026	0.024	0.040
R_w (F_o)	0.031	0.031	0.027	0.027

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper. [b] Lattice parameters calculated from Guinier powder data, using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as standard. The residuals are defined as follows: $R = (\sum|F_o - |F_c||)/\sum F_o$; $R_w = [\sum w[(F_o - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 4F^2/[\sigma(I)^2 + (0.04F^2)^2]^{1/2}$. [c] The corresponding Pearson symbols[7] are *hP*26−4.92, *hP*44−5.00, *hP*68−4.76, and *hP*98−5.02, respectively.

Well-crystallized samples of the four compounds have gray color and metallic luster, like elemental silicon. The powders are black. They deteriorate in air within a few days.

Structure Determinations

Single-crystals of the four compounds were isolated from arc-melted, annealed, crushed buttons. They had the shape of needles with the (short) hexagonal *c* axis as the preferred growth direction.

The hexagonal cells found from the Guinier powder data of $La_5Ni_{2-x}Si_3$ and $La_{21}Ni_{11-x}Si_{15}$ were confirmed by recording the reciprocal lattice in a Weissenberg camera. Single-crystal X-ray intensity data for all four compounds were collected at room temperature on Enraf-Nonius CAD4 diffractometers with κ geometry using graphite-monochromated Mo Kα radiation and a scintillation counter with pulse-height discrimination. The scans were along θ with background counts at both ends of each scan. Absorption corrections were made from ψ-scan data. The crystallographic data are summarized in Table 1 and in more detail in tables of the Supporting Information.

The structures were determined and refined with the SHELX-TL PLUS program package.[8] The final least-squares refinements were carried out with the SDP program.[9] All four structures were already approximately known from the powder data, as will be discussed further below, and therefore the positional parameters of these structure models were used as starting parameters for the full-matrix least-squares refinements using atomic scattering factors,[10] corrected for anomalous dispersion.[11] Parameters accounting for isotropic secondary extinction were optimized as least-squares parameters. The weighting schemes accounted for the counting statistics.

Occupancy parameters were refined for all atomic positions with fixed scale factors together with the thermal parameters. Most atomic positions were found to be fully occupied, and the distinction between most nickel and silicon positions could easily be made not only by their respective atomic environments but also on the basis of the refined occupancy parameters (Table 2). In the final least-squares cycles these atomic positions were refined with the ideal occupancy values.

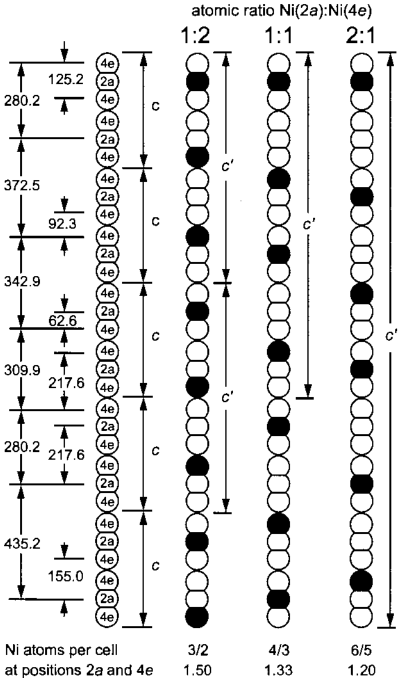

Figure 1. The distributions of nickel atoms at the positions 2*a* (0, 0, $^1/_4$) and 4*e* (0, 0, *z*) on the 6_3 axes of the lanthanum nickel silicides. As an example, the interatomic distances (pm) of $La_{21}Ni_{11-x}Si_{15}$ are indicated at the left-hand side of the figure. The occupation of two positions with interatomic distances <220 pm was considered as not possible. The translation periods *c′* at the right-hand side of the columns correspond to hypothetical models for occupied (filled) and unoccupied sites (open circles). The ratios of nickel atoms occupying the positions 2*a* and 4*e* are shown at the top of the figure; the resulting maximum number of nickel atoms per translation period *c* is indicated at the bottom.

The only difficulties arose with the atomic positions (0, 0, $^1/_4$ and 0, 0, *z*) located on the 6_3 axes with the Wyckoff notations 2*a* and 4*e* (Figure 1). Both of these sites were found to be occupied, but because the translation period *c* is rather short in all of these structures (∼435 pm), these positions cannot be fully occupied for steric reasons. The atomic environments of these positions are similar to those of the nickel and silicon atoms. The question which of the two should be favored was dealt with at length in a recent publication[12] on the closely related structures of $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$, considering

---

(8) Sheldrick, G. M. *SHELXTL PLUS*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(9) Frenz, B. A., and Associates Inc. and Enraf-Nonius. *SDP (Structure Determination Package)*, Version 3; College Station (Texas) and Delft (Holland), 1985.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(12) Prots', Yu. M.; Jeitschko, W. *J. Solid State Chem.* **1998**, *137*, 302.

Table 2. Atomic Parameters of $La_6Ni_{2-x}Si_3$, $La_5Ni_{2-x}Si_3$, $La_{15}Ni_{7-x}Si_{10}$, and $La_{21}Ni_{11-x}Si_{15}$[a]

atom	$P6_3/m$	occupancy	x	y	z	B_{eq}	CP
$La_6Ni_{1.54(2)}Si_3$							
La1	6*h*	0.999(2)	0.24140(5)	0.23084(5)	$^1/_4$	1.41(1)	**a**
La2	6*h*	1.000(2)	0.52021(5)	0.13869(5)	$^1/_4$	0.90(1)	**b**
Ni1	4*e*	0.094(4)*	0	0	0.104(4)	0.9*	**e**
Ni2	2*c*	0.994(7)	$^1/_3$	$^2/_3$	$^1/_4$	1.08(3)	**d**
Ni3	2*a*	0.355(6)*	0	0	$^1/_4$	0.9*	**f**
Si	6*h*	0.984(8)	0.1639(2)	0.4453(2)	$^1/_4$	1.01(4)	**g**
$La_5Ni_{1.75(1)}Si_3$							
La1	6*h*	1.001(2)	0.00996(4)	0.18316(5)	$^1/_4$	1.46(1)	**a**
La2	6*h*	1.001(2)	0.40055(4)	0.26433(4)	$^1/_4$	0.85(1)	**b**
La3	6*h*	1.001(2)	0.45525(4)	0.06803(4)	$^1/_4$	0.82(1)	**b**
La4	2*c*	0.999(4)	$^1/_3$	$^2/_3$	$^1/_4$	0.80(1)	**c**
Ni1	6*h*	0.974(5)	0.2821(1)	0.4991(1)	$^1/_4$	0.93(3)	**d**
Ni2	4*e*	0.083(5)*	0	0	0.114(5)	0.9*	**e**
Ni3	2*a*	0.335(8)*	0	0	$^1/_4$	0.9*	**f**
Si1	6*h*	0.97(1)	0.1677(2)	0.5522(2)	$^1/_4$	0.93(5)	**h**
Si2	6*h*	0.98(1)	0.2329(2)	0.3293(2)	$^1/_4$	1.02(6)	**g**
$La_{15}Ni_{6.62(2)}Si_{10}$							
La1	6*h*	1.004(2)	0.13183(3)	0.14868(3)	$^1/_4$	1.31(1)	**a**
La2	6*h*	1.002(2)	0.32182(3)	0.12395(3)	$^1/_4$	0.84(1)	**b**
La3	6*h*	0.997(2)	0.35616(3)	0.32177(3)	$^1/_4$	0.84(1)	**b**
La4	6*h*	0.996(2)	0.50191(3)	0.08170(3)	$^1/_4$	0.82(1)	**b**
La5	6*h*	0.996(2)	0.53400(3)	0.28881(3)	$^1/_4$	0.88(1)	**c**
Ni1	6*h*	0.989(4)	0.15420(6)	0.39517(6)	$^1/_4$	0.91(2)	**d**
Ni2	6*h*	0.998(4)	0.19972(6)	0.62056(6)	$^1/_4$	0.94(2)	**d**
Ni3	4*e*	0.156(4)*	0	0	0.090(2)	0.9*	**e**
Ni4	2*a*	0.306(6)*	0	0	$^1/_4$	0.9*	**f**
Si1	6*h*	0.979(8)	0.0623(1)	0.2584(1)	$^1/_4$	0.95(5)	**g**
Si2	6*h*	0.978(8)	0.1103(1)	0.4851(1)	$^1/_4$	0.90(5)	**h**
Si3	6*h*	0.976(8)	0.2899(1)	0.4448(1)	$^1/_4$	0.97(5)	**h**
Si4	2*c*	0.99(1)	$^1/_3$	$^2/_3$	$^1/_4$	0.77(6)	**i**
$La_{21}Ni_{10.49(3)}Si_{15}$							
La1	6*h*	0.971(4)	0.10837(7)	0.12769(8)	$^1/_4$	1.52(3)	**a**
La2	6*h*	1.009(4)	0.26894(6)	0.11175(6)	$^1/_4$	0.91(3)	**b**
La3	6*h*	1.016(4)	0.29214(6)	0.27500(6)	$^1/_4$	0.84(3)	**b**
La4	6*h*	1.003(4)	0.42280(6)	0.08350(6)	$^1/_4$	0.80(3)	**b**
La5	6*h*	1.002(4)	0.44425(6)	0.25318(7)	$^1/_4$	0.78(2)	**c**
La6	6*h*	0.992(4)	0.57502(6)	0.05055(6)	$^1/_4$	0.79(3)	**b**
La7	6*h*	1.005(3)	0.59675(8)	0.22312(8)	$^1/_4$	0.78(2)	**c**
Ni1	6*h*	1.002(8)	0.1173(1)	0.3272(1)	$^1/_4$	0.92(6)	**d**
Ni2	6*h*	0.963(9)	0.1498(1)	0.5117(1)	$^1/_4$	0.94(6)	**d**
Ni3	6*h*	1.01(1)	0.3030(1)	0.4838(1)	$^1/_4$	0.92(7)	**d**
Ni4	4*e*	0.08(1)*	0	0	0.11(1)	0.9*	**e**
Ni5	2*c*	0.97(1)	$^1/_3$	$^2/_3$	$^1/_4$	0.64(8)	**d**
Ni6	2*a*	0.34(2)*	0	0	$^1/_4$	0.9*	**f**
Si1	6*h*	0.98(2)	0.0432(3)	0.2123(4)	$^1/_4$	1.2(2)	**g**
Si2	6*h*	1.05(2)	0.0772(3)	0.3987(3)	$^1/_4$	0.5(1)	**h**
Si3	6*h*	0.95(2)	0.1117(3)	0.5848(3)	$^1/_4$	0.8(1)	**h**
Si4	6*h*	0.93(2)	0.2318(3)	0.3733(3)	$^1/_4$	0.8(1)	**h**
Si5	6*h*	1.03(2)	0.2618(4)	0.5527(4)	$^1/_4$	1.0(1)	**i**

[a] The positional parameters have been standardized with the program STRUCTURE TIDY.[14] The third column contains occupancy values which had been obtained in previous least-squares cycles. In the last cycles the ideal occupancy values (1.0) were assumed with the exception of those marked with asterisks. All atoms were refined with ellipsoidal displacement parameters. The table lists the equivalent isotropic values B_{eq} ($\times 10^4$ pm^2), where $B_{eq} = (4/3)[a^{*2}B_{11} + b^{*2}B_{22} + c^{*2}B_{33} + a^*b^* \cos\gamma\, B_{12} + a^*c^* \cos\beta\, B_{13} + b^*c^* \cos\alpha\, B_{23}]$. The only exceptions occur for those atoms where the occupancy parameters were refined in the last cycles; for these atoms the isotropic displacement parameters (marked with asterisks) were held constant. The last column indicates the coordination polyhedra CP shown in Figure 3.

interatomic distances, occupation factors resulting from refinements with nickel or silicon atoms at these positions, and chemical composition as determined by energy dispersive X-ray fluorescence analyses. All of these arguments favored the occupancy of the 2*a* and 4*e* sites with nickel atoms. This is also the case for the present four structure determinations. Certainly the occupancy of these two sites solely with silicon atoms is not possible, because not more than two silicon atoms can be placed on the 6_3 axis within one translation period for steric reasons; and when we refined these positions with the scattering factors for silicon atoms, the total occupancies for these sites were all greater than 2: 2.39(6), 2.22(8), 2.77(6), and 2.2(2) for $La_6Ni_{2-x}Si_3$, $La_5Ni_{2-x}Si_3$, $La_{15}Ni_{7-x}Si_{10}$, and $La_{21}Ni_{11-x}Si_{15}$, respectively. Furthermore, even if only two silicon atoms were placed on the 6_3 axis (an idealized situation with full occupancy of the 2*a* position and a nonoccupied 4*e* position) the silicon atoms in the resulting silicon chain would be only 218 pm apart (one-half of the translation period *c*). This distance may be compared to the considerably greater Si−Si distance of 235.2 pm in the diamond modification of elemental silicon.[13] Hence, the occupation of the 2*a* and 4*e* sites solely by silicon atoms can be ruled out for these compounds. A mixed Ni/Si occupancy seems to be possible; however, for simplicity and in analogy with our previous work[12] on $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$ we refined the 2*a* and 4*e* sites with the scattering factors of nickel atoms in the final refinement cycles. These resulted in the total occupancies of 1.09(3), 1.00(3), 1.24(3), and 0.99(8) nickel atoms on the two sites per cell of the four compounds $La_6Ni_{1.54(2)}Si_3$, $La_5Ni_{1.75(1)}Si_3$, $La_{15}Ni_{6.62(2)}Si_{10}$, and $La_{21}Ni_{10.49(3)}Si_{15}$, respectively. Since the occupancy of the 2*a* site was found to be higher than that of the 4*e* site, the atom distributions are expected to be similar to those shown in the two right-hand columns of Figure 1. The atomic parameters and interatomic distances are summarized in Tables 2 and 3 and further detailed in the Supporting Information.

Discussion

Of the two new compounds reported here, $La_{21}Ni_{11-x}Si_{15}$ crystallizes with a new structure type (Figure 2), while $La_{15}Ni_{7-x}Si_{10}$ is isotypic with $Pr_{15}Ni_7Si_{10}$.[4] As mentioned above, the other two compounds, $La_5Ni_{2-x}Si_3$ and $La_6Ni_{2-x}Si_3$, have already been reported. However, in contrast to these earlier structure determinations from film data,[1,3] we find ordered distributions of the nickel and silicon atoms in these compounds. The four structures are closely related, and they contain the same coordination polyhedra (Table 2 and Figure 3).

As an example for these four structures we will discuss that of $La_{21}Ni_{11}Si_{15}$ in more detail, since it represents a new structure type. With the exception of the nickel atoms on the Wyckoff position 4*e* (Figure 1), all atoms are located on mirror planes, which are oriented perpendicular to the hexagonal axis. The lanthanum atoms form trigonal prisms which share all of their trigonal faces and most of the rectangular faces with adjacent trigonal lanthanum prisms. The nickel and silicon atoms are located inside these trigonal prisms.

The lanthanum atoms have three different kinds of environments, designated **a**, **b**, and **c** in Figure 3, with 15 (10 La + 2 Ni + 3 Si), 17 (10 La + 2 Ni + 5 Si), and 20 (8 La + 6 Ni + 6 Si) nearest neighbors. The coordination polyhedron **a** occurs for the La1 atoms. It contains the nickel atoms Ni4 and Ni6 of the positions 4*e* and 2*a*, which are located on the 6_3 axes and which are only partially occupied. Most frequently this coordination polyhedron will contain two of these nickel atoms, and occasionally it will contain one. Within the coordination polyhedra of the lanthanum atoms the La−Si interactions are probably the most important ones, as is reflected by the interatomic distances, which correlate with the coordination numbers. The average La−Si distances are rather short for the La1 atom with 311.6 pm and three silicon neighbors. For the La2, La3, La4, and La6 atoms, which have five silicon

---

(13) Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974.

Table 3. Interatomic Distances in the Structures of $La_6Ni_{2-x}Si_3$, $La_5Ni_{2-x}Si_3$, $La_{15}Ni_{7-x}Si_{10}$, and $La_{21}Ni_{11-x}Si_{15}$[a]

$La_6Ni_{1.54}Si_3$

La1:	1Ni3*	289.3
	2Ni1*	296.3
	2Si	314.2
	1Si	320.7
	2Ni1*	328.3
	2Ni3*	362.9
	4La1	362.9
	2La2	377.1
	1La2	406.6
	1La2	409.6
	2La1	438.3
La2:	2Ni2	307.0
	2Si	317.0
	2Si	321.0
	1Si	338.2
	2La2	372.3
	2La1	377.1
	2La2	386.0
	1La1	406.6
	1La1	409.6
	2La2	438.3
Ni1:	1Ni3	283.2
	3La1	296.3
	1Ni1	310.3
	3La1	328.3
Ni2:	3Si	245.5
	6La2	307.0
Ni3:	2Ni1	283.2
	3La1	289.3
	6La1	362.9
Si:	1Ni2	245.5
	2La1	314.2
	2La2	317.0
	1La1	320.7
	2La2	321.0
	1La2	338.2

$La_5Ni_{1.75}Si_3$

La1:	1Ni3*	289.8
	2Ni2*	295.7
	2Si2	312.3
	1Si2	318.7
	2Ni2*	330.2
	4La1	362.1
	2Ni3*	362.1
	2La2	376.2
	1La3	409.8
	1La2	412.7
	2La1	434.4
La2:	2Ni1	301.7
	2Si1	312.9
	2Si2	321.6
	1Si2	337.7
	1La3	371.4
	2La1	376.2
	2La3	388.0
	1La4	388.6
	1La3	411.5
	1La1	412.7
	2La2	434.4
La3:	2Ni1	305.9
	2Si1	314.6
	2Si2	317.1
	1Si1	340.4
	1La2	371.4
	2La3	386.4
	2La2	388.0
	1La4	394.5
	1La1	409.8
	1La2	411.5
	2La3	434.4
La4:	6Si1	322.6
	6Ni1	324.9
	3La2	388.6
	3La3	394.6
	2La4	434.4
Ni1:	1Si1	239.3
	1Si1	240.9
	1Si2	245.8
	2La2	301.7
	2La3	305.9
	2La4	324.9
Ni2:	1Ni3	276.1
	3La1	295.7
	1Ni2	316.6
	3La1	330.2
Ni3:	2Ni2	276.1
	3La1	289.8
	6La1	362.1
Si1:	1Ni1	239.3
	1Ni1	240.9
	2La2	312.9
	2La3	314.6
	2La4	322.6
	1La3	340.4
Si2:	1Ni1	245.8
	2La1	312.3
	2La3	317.1
	1La1	318.7
	2La2	321.6
	1La2	337.7

$La_{15}Ni_{6.62}Si_{10}$

La1:	1Ni4*	285.0
	2Ni3*	293.4
	2Si1	312.1
	1Si1	316.4
	2Ni3*	321.2
	2Ni4*	358.6
	4La1	358.6
	2La2	375.4
	1La2	411.3
	1La3	411.5
	2La1	435.1
La2:	2Ni1	300.3
	2Si3	312.2
	2Si1	322.1
	1Si1	332.6
	1La3	370.0
	2La1	375.4
	2La3	386.9
	1La5	389.9
	1La1	411.3
	1La4	413.4
	2La2	435.1
La3:	2Ni1	305.1
	2Si2	314.3
	2Si1	317.3
	1Si3	336.1
	1La2	370.0
	2La4	386.7
	2La2	386.9
	1La5	397.0
	1La1	411.5
	1La4	412.6
	2La3	435.1
La4:	2Ni2	302.3
	2Si2	313.7
	2Si3	315.6
	1Si2	341.9
	1La5	385.2
	2La3	386.7
	1La5	390.2
	2La4	392.3
	1La3	412.6
	1La2	413.4
	2La4	435.1
La5:	2Ni2	320.1
	2Si4	321.3
	2Si3	323.0
	2Si2	323.2
	2Ni2	323.3
	2Ni1	329.1
	1La4	385.2
	1La2	389.9
	1La4	390.2
	1La3	397.0
	2La5	409.4
	2La5	435.1
Ni1:	1Si2	238.7
	1Si3	240.4
	1Si1	244.1
	2La2	300.3
	2La3	305.1
	2La5	329.1
Ni2:	1Si4	237.5
	1Si3	239.6
	1Si2	241.2
	2La4	302.3
	2La5	320.1
	2La5	323.3
Ni3:	1Ni4	287.1
	3La1	293.4
	1Ni3	296.1
	3La1	321.2
Ni4:	3La1	285.0
	2Ni3	287.1
	6La1	358.6
Si1:	1Ni1	244.1
	2La1	312.1
	1La1	316.4
	2La3	317.3
	2La2	322.1
	1La2	332.6
Si2:	1Ni1	238.7
	1Ni2	241.2
	2La4	313.7
	2La3	314.3
	2La5	323.2
	1La4	341.9
Si3:	1Ni2	239.6
	1Ni1	240.4
	2La2	312.2
	2La4	315.6
	2La5	323.0
	1La3	336.1
Si4:	3Ni2	237.6
	6La5	321.3

$La_{21}Ni_{10.49}Si_{15}$

La1:	1Ni6*	289.4
	2Ni4*	296.1
	2Si1	309.5
	1Si1	315.8
	2Ni4*	328.3
	2Ni6*	362.1
	4La1	362.1
	2La2	371.9
	1La3	409.1
	1La2	410.5
	2La1	435.2
La2:	2Ni1	300.6
	2Si4	313.8
	2Si1	323.7
	1Si1	330.3
	1La3	371.4
	2La1	371.9
	2La3	387.4
	1La5	391.0
	1La1	410.5
	1La4	412.1
	2La2	435.2
La3:	2Ni1	305.0
	2Si2	312.8
	2Si1	318.0
	1Si4	336.8
	1La2	371.4
	2La4	384.9
	2La2	387.4
	1La5	398.4
	1La1	409.1
	1La6	410.7
	2La3	435.2
La4:	2Ni3	300.2
	2Si4	313.9
	2Si3	314.0
	1Si2	341.6
	2La3	384.9
	1La7	387.4
	1La5	388.5
	2La6	393.7
	1La2	412.1
	1La6	415.4
	2La4	435.2
La5:	2Ni2	317.3
	2Si5	317.7
	2Si4	322.1
	2Ni3	323.0
	2Si2	324.7
	2Ni1	330.6
	1La6	384.8
	1La4	388.5
	1La2	391.0
	1La3	398.4
	1La7	408.8
	1La7	411.6
	2La5	435.2
La6:	2Ni2	303.2
	2Si2	313.6
	2Si3	316.9
	1Si3	344.9
	1La5	384.8
	2La6	388.4
	2La4	393.7
	1La7	395.2
	1La3	410.7
	1La4	415.4
	2La6	435.2
La7:	2Ni5	319.9
	2Si3	321.5
	2Si5	321.7
	2Ni3	323.9
	2Si5	323.9
	2Ni2	327.0
	1La4	387.4
	1La6	395.2
	2La7	406.2
	1La5	408.8
	1La5	411.6
	2La7	435.2
Ni1:	1Si2	238.0
	1Si4	242.2
	1Si1	244.8
	2La2	300.6
	2La3	305.0
	2La5	330.6
Ni2:	1Si3	237.5
	1Si5	238.3
	1Si2	240.8
	2La6	303.2
	2La5	317.3
	2La7	327.0
Ni3:	1Si5	233.9
	1Si4	235.5
	1Si3	237.9
	2La4	300.2
	2La5	323.0
	2La7	323.9
Ni4:	1Ni6	280.2
	3La1	296.1
	1Ni4	309.9
	3La1	328.3
Ni5:	3Si5	242.2
	6La7	319.9
Ni6:	2Ni4	280.2
	3La1	289.4
	6La1	362.1
Si1:	1Ni1	244.8
	2La1	309.5
	1La1	315.8
	2La3	318.0
	2La2	323.7
	1La2	330.3
Si2:	1Ni1	238.0
	1Ni2	240.8
	2La3	312.8
	2La6	313.6
	2La5	324.7
	1La4	341.6
Si3:	1Ni2	237.5
	1Ni3	237.9
	2La4	314.0
	2La6	316.9
	2La7	321.5
	1La6	344.9
Si4:	1Ni3	235.5
	1Ni1	242.2
	2La2	313.8
	2La4	313.9
	2La5	322.1
	1La3	336.8
Si5:	1Ni3	233.9
	1Ni2	238.3
	1Ni5	242.2
	2La5	317.7
	2La7	321.7
	2La7	323.9

[a] All distances shorter than 490 pm (La−La), 380 pm (La−Ni, La−Si, Ni−Si, Si−Si), and 330 pm (Ni−Ni) are listed. Standard deviations are all less than 0.7 pm. The polyhedra of the La1 atoms of all four structures contain the nickel atoms of the partially occupied sites on the 6_3 axes which are marked with asterisks. For steric reasons only one or two of these nickel sites can be occupied at the same time.

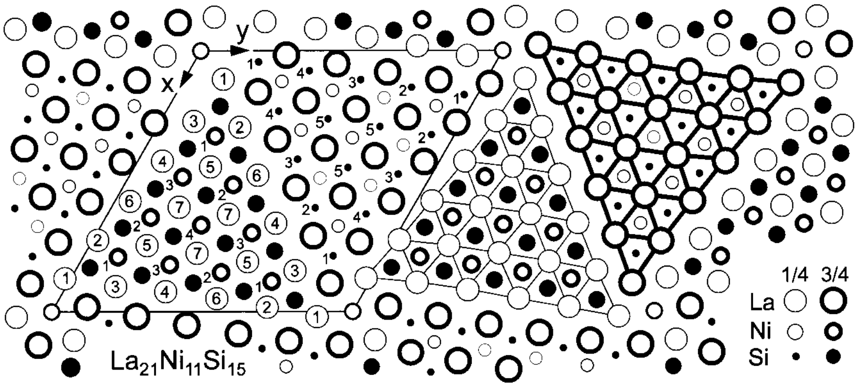

Figure 2. Projection of the $La_{21}Ni_{11-x}Si_{15}$ structure along the hexagonal axis. The numbers inside the circles represent the atom designations of the lanthanum atoms. The other atom designations in the lower left-hand and upper right-hand parts of the outlined cell correspond to the nickel and silicon atoms, respectively. In the right-hand part of the figure the trigonal prisms of lanthanum atoms surrounding the nickel and silicon atoms are emphasized.

neighbors, they are longer: 321.1, 319.7, 319.5, and 321.2 pm, respectively. And for the La5 and La7 atoms with six silicon neighbors they are the longest: 321.5 and 322.4 pm, respectively. The La−Ni interactions are certainly also bonding: the

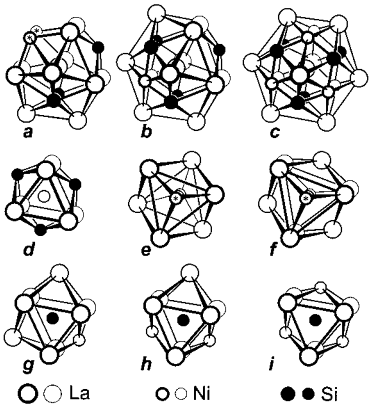

Figure 3. Coordination polyhedra occurring in the structures of $La_6Ni_2Si_3$, $La_5Ni_2Si_3$, $La_{15}Ni_7Si_{10}$, and $La_{21}Ni_{11}Si_{15}$. The symbols **a**−**i** correspond to the atom designations as indicated in Table 2. All coordination polyhedra contain mirror planes, which are oriented approximately perpendicular to the projection directions. The nickel positions on the 6_3 axes are designated with asterisks. Not all of these partially occupied positions are shown, but all corresponding interatomic distances are listed in Table 3.

corresponding distances cover the range between 300.2 and 330.6 pm for the La2−La7 polyhedra, where all nickel positions are fully occupied. The La−La distances extend between 362.1 and 435.2 pm. In view of the large lanthanum content of the compound and considering that most of these distances are similar to the average La−La distance of 375.4 pm in elemental lanthanum,[15] the La−La interactions will also contribute to the stability of the compounds.

Most nickel atoms are situated in a trigonal prism of lanthanum atoms with three silicon atoms outside the rectangular faces of that prism, thus increasing the coordination number to 9 (polyhedron **d** of Figure 3). The Ni−Si distances are all rather short. They vary between 233.9 and 244.8 pm. These values are only slightly greater than the sum of the single-bond radii (232.7 pm) for silicon (117.3 pm) and nickel (115.4 pm) given by Pauling.[16] The Ni4 and Ni6 atoms of $La_{21}Ni_{11-x}Si_{15}$ are situated on the 6_3 axis at the 4*e* and 2*a* positions, which cannot be fully occupied as already discussed. They have octahedral and tricapped trigonal prismatic lanthanum coordination with additional nickel atoms above and below (coordination polyhedra **e** and **f** in Figure 3). At first sight the coordination polyhedron **f** of the Ni6 atoms seems to violate the “waist-contact-restriction rule”, which states that transition metal atoms located in trigonal prisms of rare earth atoms should not have contact to rare earth or transition element atoms outside the rectangular faces of the prisms.[17] However, this rule is only applicable for trigonal prisms which are elongated along the trigonal axis, as is usually the case.[17,18] In contrast, the trigonal prisms of the lanthanum atoms in the coordination polyhedron **f** are compressed with an average *w/s* ratio (as defined by Parthé et al.[17]) of ∼0.87 in the four compounds, and therefore the waist-contact-restriction rule does not apply here.

The silicon atoms are also located in trigonal prisms formed by rare earth atoms with one nickel and two rare earth, two nickel and one rare earth, or with three nickel atoms outside the rectangular faces of the trigonal rare earth prisms (coordination polyhedra **g**, **h**, and **i** of Figure 3).

The crystal structures of the compounds with the idealized formulas $La_6Ni_2Si_3$, $La_5Ni_2Si_3$, $La_{15}Ni_7Si_{10}$, and $La_{21}Ni_{11}Si_{15}$ reported here belong to a large family of structures with a metal:metalloid ratio close to or exactly 2:1. Most of these are ternary compounds with two kinds of metal atoms: large, electropositive metals, e.g., lanthanoids, actinoids, and early transition elements, which we designate with the letter *R* in the present paper, and late transition metals, here designated with *T*. The most common metalloids *M* are silicon and phosphorus.[7,12,17−29] In all of these structures almost all atoms are located on two mirror planes, which extend perpendicular to the short translation period, and almost all metalloid atoms are situated in trigonal prisms formed by the *R* and/or *T* atoms.

In the lanthanum nickel silicides characterized here, not only all silicon but also most of the nickel atoms are surrounded by lanthanum atoms. These trigonal prisms are all oriented parallel to each other, and they share most of their rectangular faces, thus forming larger triangular prismatic building blocks, which are emphasized in Figure 4, where they appear as large triangles in the projections along the hexagonal axes. Each hexagonal cell has two of these triangular building blocks, which are shifted relative to each other in the *z* direction by half a translation period. The edges of the triangles forming the cross sections of the triangular building blocks consist of $n = 2$, 3, 4, and 5 lanthanum triangles in the compounds $La_6Ni_2Si_3$ (idealized cell content: $La_{12}Ni_4Si_6$), $La_5Ni_2Si_3$ ($La_{20}Ni_8Si_{12}$), $La_{15}Ni_7Si_{10}$ ($La_{30}Ni_{14}Si_{20}$), and $La_{21}Ni_{11}Si_{15}$ ($La_{42}Ni_{22}Si_{30}$), respectively. The general formula for these compounds is $R_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$. The most simple compound of this series “La_3NiSi” with $n = 1$ is not known; however, the corresponding structure has been reported for the binary compound with the idealized formula Er_3Ru_2 by Fornasini and Palenzona.[30]

Figure 4 also shows another series of hexagonal structures formed by thorium or uranium as the *R* component, late transition elements as the *T* component, and phosphorus as the component *M*. The examples chosen for our figure are Ni_2P[31] with Fe_2P type structure, $Th_2Ni_{12}P_7$[32] and $U_2Ni_{12}P_7$[33,34] with $Zr_2Fe_{12}P_7$ structure,[35] $Th_6Ni_{20}P_{13}$[32] and $U_6Ni_{20}P_{13}$[36] with $Zr_6Ni_{20}P_{13}$

---

(14) Gelato, L. M.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139.

(15) (a) Teatum, K.; Gschneidner, K. A., Jr.; Waber, J. *LA-2345*; U.S. Department of Commerce: Washington, DC, 1960. (b) Pearson, W. B. *The Crystal Chemistry and Physics of Metals and Alloys*; Wiley: New York, 1972.

(16) Pauling, L. *The Chemical Bond*; Cornell University Press: Ithaca, NY, 1967.

(17) Parthé, E.; Chabot, B.; Hovestreydt, E. *Acta Crystallogr.* **1983**, *B39*, 596.

(18) Parthé, E.; Hovestreydt, E. *J. Less-Common Met.* **1985**, *110*, 307.

(19) Yarmolyuk, Ya. P.; Aksel’rud, L. G. *Sov. Phys. Crystallogr.* **1983**, *28*, 653.

(20) Parthé, E.; Chabot, B. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1984; Vol. 6, pp 113−334.

(21) Madar, R.; Ghetta, V.; Dhahri, E.; Chaudouet, P.; Senateur, J. P. *J. Solid State Chem.* **1987**, *66*, 73.

(22) Pivan, J.-Y.; Guérin, R.; Sergent, M. *J. Solid State Chem.* **1987**, *68*, 11.

(23) Kuz’ma, Yu. B.; Chykhrii, S. I. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, 1996; Vol. 23, pp 285−434.

(24) Kuz’ma, Yu. B.; Babizhets’kii, V. S.; Chykhrii, S. I.; Oryshchyn, S. V.; Pecharskii, V. K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 587.

(25) Zimmer, B. I.; Jeitschko, W. *Z. Kristallogr.* **1994**, *209*, 950.

(26) Quebe, P.; Jeitschko, W. *J. Solid State Chem.* **1995**, *115*, 37.

(27) Albering, J. H.; Jeitschko, W. *J. Solid State Chem.* **1995**, *117*, 80.

(28) Albering, J. H.; Jeitschko, W. *J. Alloys Compd.* **1996**, *241*, 44.

(29) Chykhrii, S. I.; Babizhets’kii, V. S.; Oryshchyn, S. V.; Kuz’ma, Yu. B.; Aksel’rud, L. G. *J. Alloys Compd.* **1997**, *259*, 186.

(30) Fornasini, M. L.; Palenzona, A. *Z. Kristallogr.* **1990**, *192*, 249.

(31) Rundqvist, S.; Jellinek, F. *Acta Chem. Scand.* **1959**, *13*, 425.

(32) Albering, J. H.; Jeitschko, W. *Z. Kristallogr. Suppl.* **1993**, *7*, 5.

(33) Probst, H.; Mewis, A. *Z. Anorg. Allg. Chem.* **1991**, *597*, 173.

(34) Jeitschko, W.; Pollmeier, P. G.; Meisen, U. *J. Alloys Compd.* **1993**, *196*, 105.

(35) Ganglberger, E. *Monatsh. Chem.* **1968**, *99*, 557.

(36) Troć, R.; Kaczorowski, D.; Noël, H.; Le Bihan, T. *J. Alloys Compd.* **1992**, *184*, L27.

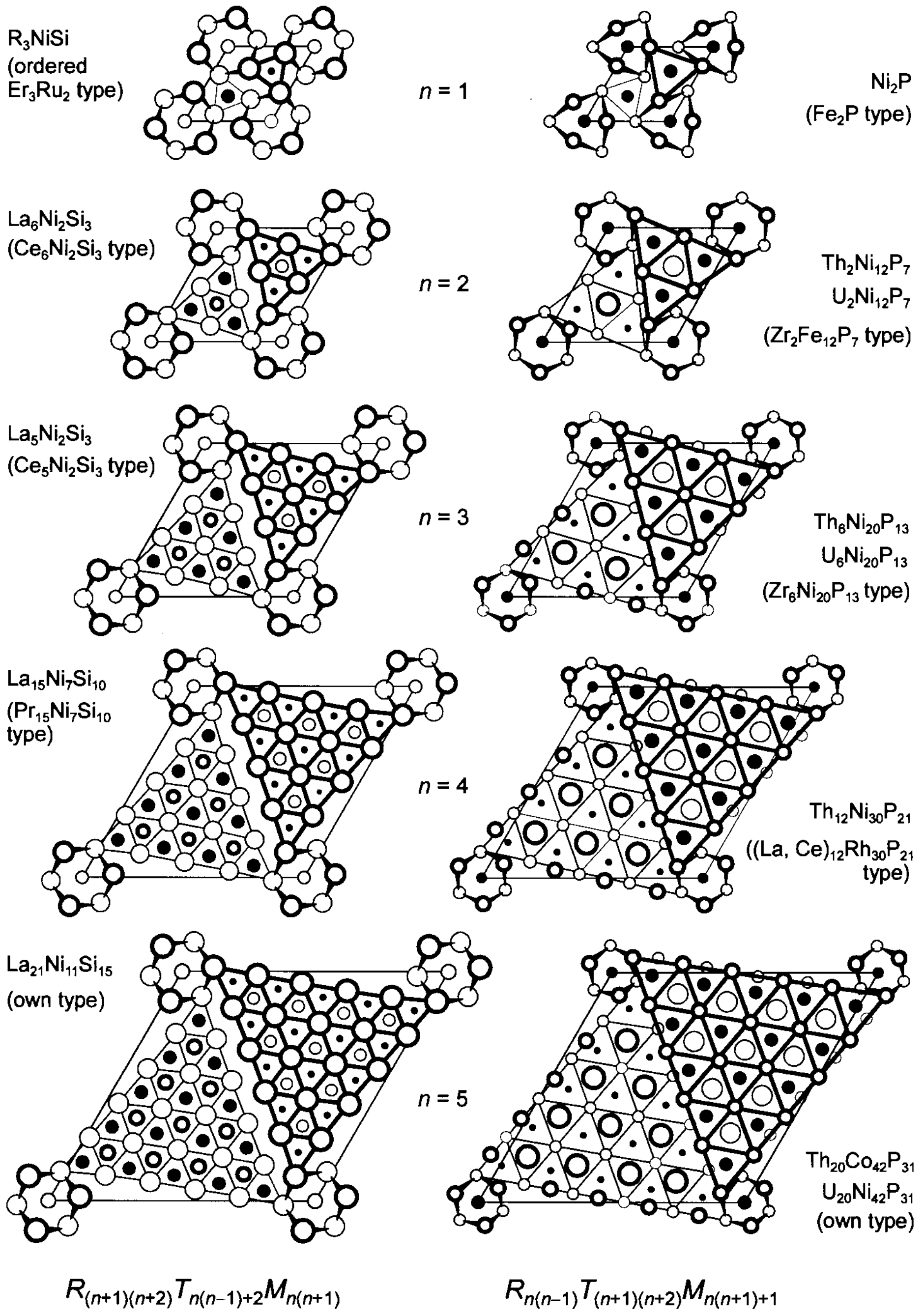

Figure 4. The compounds of two related structural series with the general formulas $R_{(n+1)(n+2)}T_{n(n-1)+2}M_{n(n+1)}$ and $R_{n(n-1)}T_{(n+1)(n+2)}M_{n(n+1)+1}$. Large open circles: La, Th, or U. Small open circles: Co or Ni. Filled circles: Si or P. The letter *n* of the general formulas indicates the number of joined trigonal prisms along one of the basal edges of the trigonal building blocks.

structure,[37] $Th_{12}Ni_{30}P_{21}$[32] with a structure first described for $(La,Ce)_{12}Rh_{30}P_{21}$,[38] and the two unpublished phosphides $Th_{20}Co_{42}P_{31}$ and $U_{20}Ni_{42}P_{31}$.[39] This series of phosphides was recognized earlier;[21,22] however, few examples were known at that time, and in some of these examples the positions at the 6_3 axis (0, 0, *z*) were reported as unoccupied.[40] The general formula of this series is $R_{n(n-1)}T_{(n+1)(n+2)}M_{n(n+1)+1}$. It can be seen that this formula is similar to the formula $R_{(n+1)(n+2)}T_{n(n-1)+2}M_{n(n+1)}$ given above for the series of lanthanum nickel silicides. The major difference between the two series results from the fact that most positions of the *R* and *T* atoms in the two series are interchanged (disregarding differences in the heights *z* of the projection direction, as discussed in the next paragraph). A minor difference is due to the occupancy of the sites 0, 0, *z* at the 6_3 (or $\bar{6}$) axes. In the silicide series the formula results from the assumption that no more than two *T* (nickel) atoms of the cell content can be situated at the positions 0, 0, *z*, whereas in the formula for the phosphides no more than one *M* (phosphorus) atom can occupy these positions. This difference results from the fact that the condensed trigonal prisms forming the major part of the cell content are composed of the (large) *R* atoms in the silicides and of the (small) *T* atoms in the phosphides. Hence, the

---

(37) Guérin, R.; El Ghadraoui, E. H.; Pivan, J.-Y.; Padiou, J.; Sergent, M. *Mater. Res. Bull.* **1984**, *19*, 1257.

(38) Pivan, J.-Y.; Guérin, R. *J. Less-Common Met.* **1986**, *120*, 247.

(39) Albering, J. *Struktur und Eigenschaften ternärer Actinoid-Übergangsmetall-Phosphide und ähnlicher Verbindungen*. Ph.D. Thesis, Universität Münster, Germany, 1994.

(40) Chykhrii, S. I.; Babizhets'kii, V. S.; Oryshchyn, S. V.; Aksel'rud, L. G.; Kuz'ma, Yu. B. *Crystallogr. Rep.* **1993**, *38*, 569.

Table 4. Systematics of Hexagonal Structures with Metal:Metalloid Ratios Close to 2:1[a]

101 $P\bar{6}m2$ 1 WC (45) BaPtSb (46)	201 $P\bar{6}m2$ 4 α-UCr_6P_4 (47)	301 $P\bar{6}m2$ 9 $Gd_4Co_{13}(Si, P)_9$ (42) $UMo_{13}P_9$ (48)	401 $P\bar{6}m2$ 16 $Ce_9Ni_{26}P_{12}$ [b](49)	501 $P\bar{6}m2$ 25 $Tb_{16}Ni_{36}P_{22}$ [b](29) $U_9Co_{37}Si_{25}$ (7)	601 $P\bar{6}m2$ 36 $Tb_{25}Ni_{49}P_{33}$ [b](29)	701 $P\bar{6}m2$ 49 $R_{36}T_{61}M_{49}$	$R_{(n-1)^2}T_{n(n+2)-2}M_{n^2}$
111 $P\bar{6}2m$ 3 Fe_2P (31) R_3TM Fe_2P (31)	211 $P\bar{6}$ 7 $Cr_{12}P_7$ (50, 51) $Ce_6Ni_2Si_3$ (3) $Zr_2Fe_{12}P_7$ (35) $T_{14}M_7$	311 $P\bar{6}$ 13 $Rh_{20}Si_{13}$ (52) $Ce_5Ni_2Si_3$ (1) $Zr_6Ni_{20}P_{13}$ (37) $R_2T_{24}M_{13}$	411 $P\bar{6}$ 21 $T_{30}M_{21}$ $Pr_{15}Ni_7Si_{10}$ (4) $(La, Ce)_{12}Rh_{30}P_{21}$ (38) $R_6T_{36}M_{21}$ $Zr_2Ni_{12}P_7$ (53)	511 $P\bar{6}$ 31 $T_{42}M_{31}$ $La_{21}Ni_{11}Si_{15}$ (54) $U_{20}Ni_{42}P_{31}$ (39) $R_{12}T_{50}M_{31}$	611 $P\bar{6}$ 43 $T_{56}M_{43}$ $R_{56}T_{32}M_{42}$ $Tb_{15}Ni_{28}P_{21}$ (40) $Ho_{20}Ni_{66}P_{43}$ (55)	711 $P\bar{6}$ 57 $T_{72}M_{56}$ $R_{72}T_{44}M_{56}$ $R_{42}T_{72}M_{57}$ $R_{30}T_{84}M_{57}$ $La_6Rh_{32}P_{17}$ (56)	$T_{(n+1)(n+2)}M_{n(n+1)+1}$ $R_{(n+1)(n+2)}T_{n(n-1)+2}M_{n(n+1)}$ $R_{n(n-1)}T_{(n+1)(n+2)}M_{n(n+1)+1}$ $R_{n(n-3)+2}T_{n(n+5)}M_{n(n+1)+1}$
	221 $P\bar{6}2m$ 12 $Hf_2Co_4P_3$ (57) $Sc_5Co_{19}P_{12}$ (58)	321 $P\bar{6}$ 19 $Yb_6Co_{30}P_{19}$ (43) $U_2Cr_{30}P_{19}$ (41, 48) $Tm_{13}Ni_{25}As_{19}$ (59)	421 $P\bar{6}$ 28	521 $P\bar{6}$ 39 $U_6Co_{30}Si_{19}$ (60)	621 $P\bar{6}$ 52	721 $P\bar{6}$ 67 $U_{10}Co_{51}Si_{33}$ (61)	
		331 $P\bar{6}2m$ 27	431 $P\bar{6}$ 37	531 $P\bar{6}$ 49 $U_6Mo_{74}P_{49}$ (41, 44)	631 $P\bar{6}$ 63	731 $P\bar{6}$ 79	
*hk*1 SG *K* *Formula (Ref.)* $K = h^2 + hk + k^2$			441 $P\bar{6}2m$ 48	541 $P\bar{6}$ 61 $Nd_{42}Ni_{22}Si_{31}$ (12)	641 $P\bar{6}$ 76	741 $P\bar{6}$ 93	

[a] For each compound the formula is listed together with the reference number (in parentheses), the *hkl* value of the strongest reflection in a powder diagram (besides the reflection 002), the space group (SG), and the corresponding *K* value as defined in the legend in the lower left-hand corner of this table. The general formulas of the series are listed in the last column. [b] The formulas $Ce_9Ni_{26}P_{12}$,[49] $Tb_{16}Ni_{36}P_{22}$,[29] and $Tb_{25}Ni_{49}P_{33}$[29] were given in the original publications. According to the structural systematics the ideal formulas are $Ce_9Ni_{22}P_{16}$, $Tb_{16}Ni_{33}P_{25}$, and $Tb_{25}Ni_{46}P_{36}$, respectively.

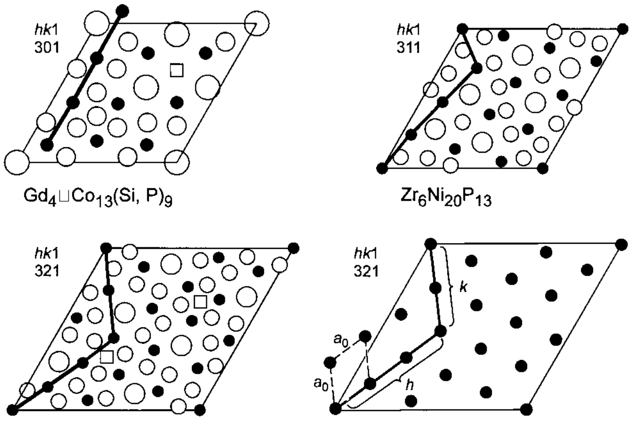

Figure 5. The lattice constants and the indices of the strongest reflections of hexagonal structures with a metal:metalloid ratio close to 2:1. The metalloid atoms (filled circles) form a hexagonal sublattice with the cell constant a_0. The cell constant of the real hexagonal cell is defined by the equation $a = a_0K^{1/2}$, where $K = h^2 + hk + k^2$ and where *h* and *k* are at the same time the indices of the strongest reflection *hk*1. *K* also equals the number of metalloid atoms in the hexagonal cell of the ideal structures. Occasionally some of the metalloid positions are occupied by late transition metal atoms, and sometimes a few metal positions are unoccupied. In the latter case these positions are indicated by the symbol □.

translation period *c* is greater in the silicides than in the phosphides. In reality there are fewer than two nickel atoms (but more than one) per translation period on the 6-fold axis in the silicides, as was discussed above.

The structures of the two series of Figure 4 were drawn emphasizing the similarities. There is another major difference between the two series. At first sight it may seem that the same atomic positions are occupied in the two series. This, however, is not the case. In the series of silicides on the left-hand side of the figure, the atoms (Ni and Si) filling the condensed trigonal prisms formed by the lanthanum atoms are at the same height of the projection direction. In each half of the hexagonal cell they form a hexagonal net similar to the net of B atoms in the AlB_2 type structure. In contrast, the *R* and phosphorus atoms occupying the condensed trigonal prisms of *T* atoms in the phosphide series are alternating in height with $\Delta z = {}^1/_2$.

Most of the X-ray powder patterns of the compounds shown in Figure 4 show two very strong diffraction lines. One is the reflection 002, and this is readily rationalized, since almost all atoms of these compounds are situated on two mirror planes, which are oriented perpendicular to the hexagonal *c* axis at $z = 0$ and $z = {}^1/_2$ or at $z = {}^1/_4$ and $z = {}^3/_4$. Hence, for the reflection 002 almost all atoms scatter in phase. The indices of the other strong reflection have been recognized empirically to be related to the size of the hexagonal cell by several authors.[19,29,41] This is shown in Figure 5 using $Gd_4Co_{13}(Si, P)_9$,[42] $Zr_6Ni_{20}Si_{13}$,[37] and $Yb_6Co_{30}P_{19}$[43] as examples, where the indices of these strongest reflections are 301, 311, and 321, respectively. Generally, the index *l* of these reflections is always 1, while the indices *h* and *k* can be extracted from the unit cell in a manner as is shown in Figure 5. The lattice constant *a* is also related to these *h* and *k* values. It is defined by the equation $a = a_0\ K^{1/2}$, where $K = h^2 + hk + k^2$. The value *K* is at the same time the number of atoms situated in the centers of the trigonal prisms formed by the metal atoms. In the examples of Figure 5 the values of *K* are 9, 13, and 19 phosphorus (silicon) atoms, respectively. These atoms form a hexagonal sublattice with a_0 as the translation period. The reader may choose the phosphide $Th_{20}Co_{42}P_{31}$[39] ($Z = 1$) of Figure 4 as another example. It can be extracted from that figure that $h = 5$ and $k = 1$. Hence, the strongest reflection of the type *hk*1 in the powder diagram has the indices 511, and there are $K = 5^2 + (5)(1) + 1 = 31$ phosphorus atoms in the cell.

---

(41) Brink, R. *Strukturchemische Untersuchungen von Phosphiden des Urans mit Chrom oder Molybdän.* Ph.D. Thesis, Universität Münster, Germany, 1989.
(42) Jakubowski-Ripke, U.; Jeitschko, W. *Z. Kristallogr.* **1987**, *178*, 116.
(43) Jeitschko, W.; Jakubowski-Ripke, U. *Z. Kristallogr.* **1993**, *207*, 69.

As examples for the calculation of the lattice constants a from the subcell lattice constant a_0 we take the series of the phosphides shown in Figure 4: Ni_2P (Ni_6P_3), $Th_2Ni_{12}P_7$, $Th_6Ni_{20}P_{13}$, $Th_{12}Ni_{30}P_{21}$, and $Th_{20}Co_{42}P_{31}$, where $K = h^2 + hk + k^2$ equals 3, 7, 13, 21, and 31, respectively. The average a_0 of the hexagonal subcell of these phosphides is close to 360 pm, and the lattice constants a calculated from the relation $a = a_0 K^{1/2}$ are 952, 1297, 1649, and 2004 pm, as compared to the observed values 911, 1281, 1669, and 2060 pm. The analogous relationship exists also for the series of lanthanum nickel silicides of Figure 4: $La_6Ni_2Si_3$ (cell content $La_{12}Ni_4Si_6$), $La_5Ni_2Si_3$ ($La_{20}Ni_8Si_{12}$), $La_{15}Ni_7Si_{10}$ ($La_{30}Ni_{14}Si_{20}$), and $La_{21}Ni_{11}Si_{15}$ ($La_{42}Ni_{22}Si_{30}$). For these compounds the number of silicon atoms per cell is $K - 1$, since the small atoms at the positions 0, 0, z are nickel instead of silicon atoms. The average a_0 of the hexagonal subcell of these silicides is close to 445 pm, and the lattice constants a calculated from the relation $a = a_0 K^{1/2}$ are 1177, 1604, 2039, and 2478 pm as compared to the observed values 1224, 1624, 2021, and 2428 pm. In both the phosphide and the silicide series there are systematic differences between the calculated and observed lattice constants a. These result from the varying Th:Ni and La:Ni ratios, respectively. If these are taken into account, the agreement is much better, and in fact the powder patterns of the compounds of $U_4Mo_{37}P_{25}$,[41] $U_6Mo_{60}P_{39}$,[41,44] $U_{12}Mo_{102}P_{67}$,[41,44] $U_6Mo_{74}P_{49}$,[41,44] and $U_{20}Ni_{42}P_{31}$[39] have been indexed on the basis of such structural systematics. Subsequently the predicted structures of $U_6Mo_{74}P_{49}$ and $U_{20}Ni_{42}P_{31}$ were refined from single-crystal[41,44] and powder diffractometer data,[39] respectively. Similarly, the model for the successfully refined structure of the presently reported silicide $La_{21}Ni_{11}Si_{15}$ was proposed by extrapolation of the recognized structural relationships shown in Figure 4.

Another regularity concerns the occupancy of the site 2c ($^1/_3$, $^2/_3$, $^1/_4$) of the silicide series $R_{(n+1)(n+2)}T_{n(n-1)+2}M_{n(n+1)}$ and the corresponding site in the phosphide series $R_{n(n-1)}T_{(n+1)(n+2)}M_{n(n+1)+1}$ of Figure 4. In the silicide series this site is occupied alternatingly with Si, Ni, La, Si, Ni, La... atoms for $n = 1, 2, 3, 4, 5, 6$..., while in the phosphide series the corresponding sites are occupied by P, Th, Ni, P, Th, Ni... atoms, respectively.

In Table 4 we have made an attempt to list all hexagonal structures which follow those structural systematics, which we have discussed above with the aid of Figure 5. The examples shown in Figure 4 are listed in lines 5 and 6 of that table. In the last column of that table the general formula is listed for those series where more than one example is known. The other examples, e.g., $UMo_{13}P_9$[41,49], $U_9Co_{37}Si_{25}$,[7] $Zr_2Cr_{12}P_7$,[53] or $La_6Rh_{32}P_{17}$,[56] belong to structural series where there is only one representative, and we have not attempted to list the general formula. The only exception is the series with $Ho_{20}Ni_{66}P_{43}$[55] as example, for which Kuz'ma and Chykhrii[23] have already given a general formula and the compositions of the hypothetical examples.

The space groups of the compounds listed in Table 4 also show some systematics. The compounds listed in lines 2 and 3 have the reflection $h01$ as a very strong reflection, and their space group is $P\bar{6}m2$. The compounds with the very strong reflections $hh1$ all crystallize with the space group $P\bar{6}2m$. Finally all other compounds are listed here with the space group $P\bar{6}$. This space group is correct when the atoms at the positions 0, 0, z are fully ordered. Frequently this is not the case, and then these structures are better refined in the space group $P6_3/m$. This has been discussed in detail elsewhere.[43]

Acknowledgment. We thank Dipl. Ing. U. Ch. Rodewald for the collection of the single-crystal diffractometer data, Mr. K. Wagner for the work at the scanning electron microscope, and Dr. G. Höfer (Heraeus Quarzschmelze) for a generous gift of silica tubes. Yu.M.P. is indebted to the Deutscher Akademischer Austauschdienst (DAAD) and the Heinrich Hertz-Stiftung for research stipends. This work was also supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Listings of the crystallographic data of $La_6Ni_{2-x}Si_3$, $La_5Ni_{2-x}Si_3$, $La_{15}Ni_{7-x}Si_{10}$, and $La_{21}Ni_{11-x}Si_{15}$ including anisotropic displacement parameters (Tables S1 and S2) (3 pages). Ordering information is given on any current masthead page.

IC980397W

---

(44) Brink, R.; Jeitschko, W. *Z. Kristallogr.* **1988**, *182*, 46.

(45) Parthé, E.; Sadagopan, V. *Monatsh. Chem.* **1962**, *93*, 263.

(46) Wenski, G.; Mewis, A. *Z. Anorg. Allg. Chem.* **1986**, *535*, 110.

(47) Jeitschko, W.; Brink., R., *Z. Naturforsch.* **1992**, *47b*, 192.

(48) Brink, R.; Jeitschko, W. *Z. Kristallogr.* **1987**, *178*, 34.

(49) Babizhets'kii, V. S.; Chykhrii, S. I.; Oryshchyn, S. V.; Kuz'ma, Yu. B. *Russ. J. Inorg. Chem.* **1992**, *37*, 1372.

(50) Baurecht, H. E.; Boller, H.; Nowotny, H. *Monatsh. Chem.* **1971**, *102*, 373.

(51) Chun, H. K.; Carpenter, G. B. *Acta Crystallogr.* **1979**, *B35*, 30.

(52) Engström, I. *Acta Chem. Scand.* **1965**, *19*, 1924.

(53) Pollmeier, P.; Albering, J. H.; Jeitschko, W. *Z. Kristallogr. Suppl.* **1997**, *12*, 242.

(54) This work.

(55) Pivan, J.-Y.; Guérin, R.; Sergent, M. *Mater. Res. Bull.* **1985**, *20*, 887.

(56) Pivan, J.-Y.; Guérin, R.; Pena, O.; Padiou, J.; Sergent, M. *Mater. Res. Bull.* **1988**, *23*, 513.

(57) Ganglberger, E. *Monatsh. Chem.* **1968**, *99*, 566.

(58) Jeitschko, W.; Reinbold, E. J. *Z. Naturforsch.* **1985**, *40b*, 900.

(59) Terbüchte, L. J.; Jeitschko, W. *Z. Kristallogr.* **1989**, *186*, 291.

(60) Yarmolyuk, Ya. P.; Aksel'rud, L. G.; Fundamenskii, V. S.; Gladyshevskii, E. I. *Sov. Phys. Crystallogr.* **1980**, *25*, 97.

(61) Aksel'rud, L. G.; Yarmolyuk, Ya. P.; Gladyshevskii, E. I. *Dopov. Akad. Nauk Ukr. RSR* **1980**, *42A*, 79.