The Neodymium Nickel Silicides $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$

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The title compounds were prepared by reaction of cold-pressed pellets of the elemental components in an arc-melting furnace followed by annealing at 900°C. Their crystal structures were determined from single-crystal X-ray data. $Nd_{42}Ni_{22-x}Si_{31}$ crystallizes with a new structure type: $P6_3/m$, $a = 3399.2(4)$ pm, $c = 417.88(8)$ pm, $Z = 2$, $R = 0.030$ for 2083 structure factors and 192 variable parameters. The neodymium atoms occupy 14 different sites with between 2 and 6 Ni, 3 and 6 Si, and 8 and 10 Nd neighbors with coordination numbers varying between 15 and 20. The nickel atoms occupy 9 sites: 7 of these have coordination number 9, with 6 Nd neighbors forming a trigonal prism and 3 Si neighbors capping the rectangular faces of that prism; 2 nickel sites on the hexagonal axis have the ideal occupancies of 25% assuming all sterically allowed sites to be occupied, resulting in the ideal composition $Nd_{42}Ni_{21.75}Si_{31}$ and the Pearson formula $hP189.5$. One of these nickel atoms has 9 Nd neighbors forming a tricapped trigonal prism with 2 additional Ni neighbors capping the trigonal faces of the prism, while the other one has octahedral Nd coordination with 2 additional Ni atoms on the 6_3 axis. The 11 different silicon sites all have ninefold coordination: a trigonal prism of 6 Nd neighbors capped by 3 Ni, 2 Ni, and 1 Nd, or 1 Ni and 2 Nd atoms. $Nd_{42}Ni_{22-x}Si_{31}$ contains building blocks of the CrB and $Ce_5Ni_2Si_3$ type structures. The structure of $Nd_6Ni_{2-x}Si_3$ ($P6_3/m$, $a = 1193.4(2)$ pm, $c = 426.8(1)$ pm, $Z = 2$, Pearson formula $hP21.5$, $R = 0.028$ for 671 F values and 25 variables) is similar to the previously reported structure of $Ce_6Ni_2Si_3$. It is also closely related to the structure of $Nd_{42}Ni_{22-x}Si_{31}$. A series of homologous rare earth (R)–transition metal (T)–main group element (or metametal, M) compounds is predicted with the general formula $R_{3(n^2+5n+4)}$ $T_{3(n^2+n+2)+2(1-x)}M_{3(n^2+3n+2)+2}$, of which $Nd_{84}Ni_{44-2x}Si_{62} \Rightarrow$ $Nd_{42}Ni_{22-x}Si_{31}$ is the member with $n = 3$. © 1998 Academic Press

INTRODUCTION

The ternary system neodymium–nickel–silicon has not yet been investigated systematically. Nevertheless, many neodymium nickel silicides are known: $NdNi_{\sim 7}Si_{\sim 6}$

($NaZn_{13}$ type) (1), $NdNi_{8.6}Si_{2.4}$ ($BaCd_{11}$ type) (2), $NdNi_2Si_2$ ($CeGa_2Al_2$ type) (3), $NdNiSi_2$ ($CeNiSi_2$ type) (4), $Nd_3Ni_6Si_2$ (Ca_3Ag_8 type) (5), $NdNiSi$ (α-$ThSi_2$ type) (6), $Nd(Ni_{0.5}Si_{1.5})_2$ (AlB_2 type) (6, 7), $Nd_6Ni_7Si_4$ ($Pr_6Ni_7Si_4$ type) (8), and $Nd_6Ni_2Si_3$ ($Ce_6Ni_2Si_3$ type) (9). Many of these compounds are isotypic with the corresponding compounds of the ternary system cerium–nickel–silicon, for which two isothermal sections are reported (10, 11). The three hexagonal compounds with the highest content of cerium—$Ce_6Ni_2Si_3$ (9), $Ce_5Ni_2Si_3$ (12–14), and $Ce_{15}Ni_4Si_{13}$ (15)—form a series of related structures with the general formula R_{n^2+3n+2} $T_{n^2-n+2}M_{n^2+n}$ (13, 15, 16). The previously characterized silicide $Nd_6Ni_2Si_3$ (9) may also be considered as belonging to this series. It has been reported to be isotypic with $Ce_6Ni_2Si_3$ (9). The structure of the latter compound, solved from film data, has been described with a disordered nickel and silicon distribution. Our present structure refinement of the corresponding neodymium compound resulted in the composition $Nd_6Ni_{1.66}Si_3$ with an ordered distribution of the nickel and silicon atoms.

Recently we have reported on the crystal structure of the new compound $La_{21}Ni_{11}Si_{15}$, which also belongs to this structural series $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ (16, 17). It is the first member with $n = 5$. Attempts to obtain an isotypic compound with neodymium as the lanthanoid component have failed. Instead we have found the new compound $Nd_{42}Ni_{22-x}Si_{31}$, which is also the subject of the present publication. Its structure is closely related to the structures of the above-mentioned series, however, it is not a member of that series.

Our structure determinations resulted in the ideal compositions $Nd_{42}Ni_{21.75}Si_{31}$ and $Nd_6Ni_{1.75}Si_3$. The actual compositions for the two crystals used for the structure determinations are very likely close to $Nd_{42}Ni_{21.67}Si_{31}$ and $Nd_6Ni_{1.66}Si_3$; however, for most purposes, we use the more general formulas $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$.

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

Starting materials were filings of neodymium ($>99.9\%$) and powders of nickel and silicon ($>99.99\%$). The rare

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earth metal filings were kept under dried paraffin oil, which was washed away by dry (Na) cyclohexane prior to the reactions. Mixtures of the components were cold-pressed to pellets of about 0.5 g and reacted in an arc-melting furnace under an argon atmosphere. The arc-melted buttons were subsequently enclosed in evacuated silica tubes and annealed for 2 weeks at 800°C. The X-ray powder diagrams indicated two new phases in the alloy with the approximate composition $\sim Nd_{45}Ni_{25}Si_{30}$, one with a new powder pattern and the other with a pattern similar to that of $Ce_6Ni_2Si_3$ (9).

The crystals of the new phases are gray with metallic luster. The powders are black. They react with the humidity of the air, whereas large crystals are relatively stable in air. Energy-dispersive X-ray analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

Apparently the compounds are somewhat ductile, since the powder diagrams showed some diffuseness. Sharp diffraction patterns were obtained after the powders had been annealed for 3 hr in a tantalum foil, which had been sealed in an evacuated silica tube. The Guinier powder diagrams were recorded with α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The indices could eventually be assigned on the basis of the hexagonal cells found during the single-crystal investigations. The identification of the diffraction lines was ensured by intensity calculations using the LAZY PULVERIX program (18) and the positional parameters of the refined structures. The lattice constants (Table 1) were obtained from least-squares fits of powder patterns recorded from samples with the ideal composition, annealed at 800°C. They are in good agreement with those obtained from the single-crystal diffractometer data. The latter were determined from reflections measured at 2θ values $> 31°$.

STRUCTURE DETERMINATIONS

The single crystals used for the structure determinations of $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$ were isolated from crushed samples of the compositions 50/25/25 and 55/15/30, respectively, which had been annealed at 800°C.

X-ray diffraction intensity data for both compounds were collected on an Enraf-Nonius four-circle diffractometer (CAD4) with a graphite monochromator using $MoK\alpha$ radiation and a scintillation counter with pulse-height discrimination. The background was determined at both sides of each $\theta/2\theta$ scan. The deviations of two standard reflections for each measurement were less than 0.5%. Absorption corrections were based on ψ scan data. Further details of the data collections and the structure refinements are given in Table 1.

Both crystals showed the Laue symmetry $6/m$ and both structures could eventually be refined in the space group

TABLE 1
Crystal Data for $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$[a]

Structure type	$Nd_{42}Ni_{22-x}Si_{31}$	$Ce_6Ni_{2-x}Si_3$
Composition	$Nd_{42}Ni_{21.67(2)}Si_{31}$	$Nd_6Ni_{1.66(1)}Si_3$
Crystal dimensions (μm^3)	$20 \times 20 \times 80$	$10 \times 15 \times 20$
Space group	$P6_3/m$ (No. 176)	$P6_3/m$ (No. 176)
Lattice constants from powder data		
a (pm)	3399.2(4)	1193.4(2)
c (pm)	417.88(8)	426.8(1)
V (nm³)	4.181(1)	0.5265(2)
Lattice constants from single-crystal data		
a (pm)	3399.0(4)	1193.9(1)
c (pm)	417.83(1)	426.6(1)
V (nm³)	4.1805(7)	0.5267(2)
Formula units/cell	$Z = 2$	$Z = 2$
Formula mass	8201	1047.1
Calculated density (g/cm³)	6.51	6.60
$\theta/2\theta$ scans up to	$2\theta = 63°$	$2\theta = 70°$
Range in hkl	$-43 \leq h \leq 49$	$-19 \leq h \leq 19$
	$-49 \leq k \leq 24$	$-19 \leq k \leq 19$
	$0 \leq l \leq 6$	$0 \leq l \leq 5$
Absorption correction	from ψ scans	from ψ scans
Highest/lowest transmission	1.68	2.21
Inner residual	0.077	0.038
Total number of reflections	18444	4773
Unique reflections	5168	1597
Reflections with $I > 2\sigma(I)$	2083	671
Number of variables	192	25
Highest residual electron density (e/Å³)	3.00	2.45
Conventional residual	$R = 0.030$	$R = 0.028$
Weighted residual	$R_w = 0.037$	$R_w = 0.035$

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

$P6_3/m$, the highest symmetric group compatible with the only extinction condition (00l observed only with $l = 2n$). Both structures were solved with the aid of the SHELXTL program package (19). The positions of some neodymium atoms were obtained by direct methods and the other atoms were located by difference Fourier syntheses. The structures were refined by the full-matrix least-squares program contained in the SDP system (20). The atomic scattering factors, corrected for anomalous dispersion, were also provided by that program. Parameters accounting for isotropic secondary extinction were optimized and the weighting schemes reflected the counting statistics.

The atomic positions $2a$ and $4e$ located on the 6_3 axes required special attention in both structures. In both structures these positions were found with considerable deviations from the ideal occupancies and this is readily rationalized, since these positions are too close to each other. In Fig. 1 we demonstrate that only every fourth of these positions can be occupied and therefore the ideal occupancies of these positions are 25%. The environments
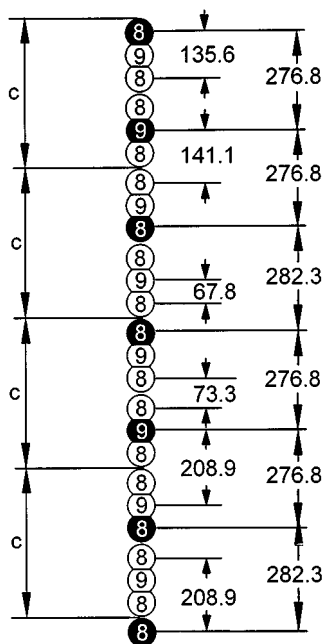
FIG. 1. Location of the Ni8 and Ni9 atoms on the hexagonal axis of the $Nd_{42}Ni_{22-x}Si_{31}$ structure. Because of the space limitations only every fourth position for these atoms can be occupied. Therefore the ideal occupancy values for these sites are 25% as is discussed in the text. This is also the case for the Ni1 and Ni3 atoms in the structure of $Nd_6Ni_{2-x}Si_3$.

of these positions—aside from the atomic sites above and below—are formed by neodymium atoms, and at first sight both nickel and silicon atoms seemed to be suited for these positions. We have placed silicon atoms on these sites and refined their occupancy values with the thermal parameters always fixed at $B = 0.8$ Å^2 (the average parameter found for the light atoms in both structures) and this resulted in occupancy values (in %) of 56(3) and 46(2) for the 2a and 4e positions in $Nd_{42}Ni_{22-x}Si_{31}$, respectively, and the values 60(1) and 45(1) for the same positions in $Nd_6Ni_{2-x}Si_3$. Hence, these values are all too high and the occupancy of these positions only with silicon atoms can definitely be ruled out. When only nickel atoms were placed at these positions, the refinements resulted in occupancy values of (in the sequence as listed above) 25(1), 20.7(8), 26.4(7), and 20.3(6). Therefore, in the final runs the nickel atoms of the 2a positions were refined with the ideal occupancies of 25%, whereas the nickel atoms of the 4e positions were refined with fixed B values and variable occupancy, resulting in the compositions $Nd_{42}Ni_{21.67(2)}Si_{31}$ and $Nd_6Ni_{1.66(1)}Si_3$. When mixed occupancies were refined for the 4e positions, we obtained Ni/Si ratios of 17.8(9)/7.2(9) and 16.8(9)/8.2(9) for the compounds, which now would have the corresponding compositions $Nd_{42}Ni_{21.61(2)}Si_{31.14(2)}$ and $Nd_6Ni_{1.59(2)}Si_{3.16(2)}$, respectively. For simplicity, we describe the structures only with nickel atoms on the positions

2a and 4e, although a mixed Ni/Si occupancy of these sites cannot be ruled out. Assuming only nickel atoms on the 2a and 4e positions with maximal occupancy, the "ideal" formulas of the two compounds are $Nd_{42}Ni_{21.75}Si_{31}$ and $Nd_6Ni_{1.75}Si_3$ and the corresponding Pearson formulas (21, 22) for these compounds are $hP194 - 4.5$ ($\sim hP189.5$) and $hP26 - 4.5$ ($\sim hP21.5$).

With the exception of these two sites of both structures, all atoms were refined with anisotropic displacement parameters. In separate series of least-squares cycles the occupancy values of these other atoms were allowed to vary together with the thermal parameters and with fixed scale factors for both structures. None of these occupancy values was off by more than 0.4% of the ideal occupancy of 100%, and in the final least-squares cycles the ideal occupancy values were resumed for these sites.

Final difference Fourier analyses showed no significant electron densities (Table 1) at sites suited for additional atomic positions. The settings of both structures were standardized by the program STRUCTURE TIDY (23). The anisotropic thermal parameters and the structure factors are available from the authors. The final residual values, the atomic parameters, and the interatomic distances are listed in Tables 1–4. Projections of both structures and the coordination polyhedra are shown in Figs. 2–4.

DISCUSSION

The crystal structure of $Nd_{42}Ni_{22-x}Si_{31}$ represents a new structure type. With the exception of the atoms at the sites 2a and 4e, located on the 6_3 axis, all atoms are situated on two mirror planes, which are oriented perpendicular to the short translation period c. The atoms occupy 34 different atomic sites, however, many of these have very similar coordination polyhedra, as can be seen from Fig. 4 and the last column of Table 2. As could be expected from the high metal content of this compound, all atoms have high coordination numbers, as is typical for intermetallic phases.

The neodymium atoms occupy 14 sites with between two and six nickel, between three and six silicon, and between eight and ten neodymium neighbors. The coordination numbers (CN) of the neodymium atoms vary between 15 and 20. The Nd–Nd distances cover the range between 350 and 418 pm with a weighted average distance of 393.2 pm. This distance is somewhat greater than twice the (metallic) radius of neodymium for CN 12 of 364.2 pm (25). The Nd–Ni distances vary between 281 and 321 pm (not counting the Nd–Ni distances of 350 and 394 pm involving the disordered nickel atoms Ni8 and Ni9 on the sixfold axis) with an average of 304.0 pm, which is slightly smaller than the sum of the radii for CN 12 of 306.7 pm. Similarly, the Nd–Si distances cover the range between 294 and 343 pm with an average of 311.6 pm, again somewhat smaller than the sum of the radii of 314.0 pm (24). Certainly, strong

TABLE 2
Atomic Parameters of $Nd_{42}Ni_{21.67(2)}Si_{31}$ and $Nd_6Ni_{1.66(1)}Si_3$

	$P6_3/m$	x	y	z	B^a	CP^b
		$Nd_{42}Ni_{21.67(2)}Si_{31}$				
Nd1	6h	0.02878(3)	0.09313(3)	$\frac{1}{4}$	1.05(2)	a
Nd2	6h	0.03241(3)	0.47939(3)	$\frac{1}{4}$	0.70(2)	b
Nd3	6h	0.11017(3)	0.23011(3)	$\frac{1}{4}$	0.76(2)	c
Nd4	6h	0.16632(3)	0.16275(3)	$\frac{1}{4}$	0.76(2)	c
Nd5	6h	0.17239(3)	0.54461(3)	$\frac{1}{4}$	0.70(2)	d
Nd6	6h	0.18739(3)	0.36719(3)	$\frac{1}{4}$	0.69(2)	c
Nd7	6h	0.24207(3)	0.29203(3)	$\frac{1}{4}$	0.77(2)	e
Nd8	6h	0.26183(3)	0.50259(3)	$\frac{1}{4}$	0.66(2)	f
Nd9	6h	0.30430(3)	0.22426(3)	$\frac{1}{4}$	0.72(2)	c
Nd10	6h	0.31789(3)	0.42930(3)	$\frac{1}{4}$	0.72(2)	g
Nd11	6h	0.38060(3)	0.35373(3)	$\frac{1}{4}$	0.74(2)	g
Nd12	6h	0.44385(3)	0.28621(3)	$\frac{1}{4}$	0.76(2)	h
Nd13	6h	0.52186(3)	0.10771(3)	$\frac{1}{4}$	0.71(2)	i
Nd14	6h	0.60607(3)	0.25935(3)	$\frac{1}{4}$	0.67(2)	j
Ni1	6h	0.02263(8)	0.31055(8)	$\frac{1}{4}$	0.88(5)	k
Ni2	6h	0.09907(8)	0.44894(8)	$\frac{1}{4}$	0.81(5)	k
Ni3	6h	0.22377(8)	0.05526(8)	$\frac{1}{4}$	0.81(5)	k
Ni4	6h	0.27254(8)	0.59358(8)	$\frac{1}{4}$	0.73(5)	k
Ni5	6h	0.36313(8)	0.11507(8)	$\frac{1}{4}$	0.83(5)	k
Ni6	6h	0.42497(8)	0.04008(8)	$\frac{1}{4}$	0.84(5)	k
Ni7	6h	0.50402(8)	0.17990(8)	$\frac{1}{4}$	0.80(5)	k
Ni8^c	4e	0	0	0.086(4)	0.80*	l
Ni9^c	2a	0	0	$\frac{1}{4}$	1.0(3)	m
Si1	6h	0.0178(2)	0.2369(2)	$\frac{1}{4}$	1.1(1)	n
Si2	6h	0.0387(2)	0.5785(2)	$\frac{1}{4}$	0.7(1)	n
Si3	6h	0.0959(2)	0.3765(2)	$\frac{1}{4}$	0.9(1)	n
Si4	6h	0.1556(2)	0.0618(2)	$\frac{1}{4}$	0.9(1)	o
Si5	6h	0.2965(2)	0.1225(2)	$\frac{1}{4}$	0.7(1)	n
Si6	6h	0.3587(2)	0.0448(2)	$\frac{1}{4}$	0.8(1)	p
Si7	6h	0.3608(2)	0.5412(2)	$\frac{1}{4}$	0.9(1)	n
Si8	6h	0.4342(2)	0.1822(2)	$\frac{1}{4}$	1.0(1)	n
Si9	6h	0.5557(2)	0.3142(2)	$\frac{1}{4}$	0.8(1)	n
Si10	6h	0.6125(2)	0.0997(2)	$\frac{1}{4}$	0.7(1)	n
Si11	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.6(1)	p
		$Nd_6Ni_{1.66(1)}Si_3$				
Nd1	6h	0.24038(3)	0.22947(3)	$\frac{1}{4}$	0.982(7)	a
Nd2	6h	0.51988(3)	0.13899(3)	$\frac{1}{4}$	0.683(6)	c
Ni1^c	4e	0	0	0.091(1)	0.80*	l
Ni2	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.85(2)	k
Ni3^c	2a	0	0	$\frac{1}{4}$	0.88(9)	m
Si	6h	0.1607(2)	0.4423(2)	$\frac{1}{4}$	0.79(4)	o

^{a}Most atoms were refined with anisotropic displacement parameters. Here the equivalent isotropic parameters are listed in units of 10^4 pm^2 (Å^2). The atoms located on the positions 2a and 4e were refined with isotropic thermal parameters. The thermal parameters marked with asterisks were held constant.

^{b}The last column indicates the kind of coordination polyhedra (CP), which are shown in Fig. 4.

^{c}The ideal occupancy values of the Ni8 and Ni9 positions of $Nd_{42}Ni_{22-x}Si_{31}$ and of the Ni1 and Ni3 positions in $Nd_6Ni_{2-x}Si_3$ are 25%, corresponding to the ideal formulas $Nd_{42}Ni_{21.75}Si_{31}$ and $Nd_6Ni_{1.75}Si_3$. In the final runs the occupancy values of these Ni9 and Ni3 positions were held at these ideal values, as discussed in the text. For the Ni8 and Ni1 positions they were refined and found to be 20.7(8) and 20.3(6)%, respectively. The resulting compositions are $Nd_{42}Ni_{21.67(2)}Si_{31}$ and $Nd_6Ni_{1.66(1)}Si_3$.

Nd–Si bonding can be assumed, and in view of the high metal content of the compounds and the high coordination numbers, we also assume considerable Nd–Ni and somewhat less Nd–Nd bonding.

The nickel atoms on the Wyckoff positions 6h are situated in trigonal prisms formed by neodymium atoms. The three rectangular faces of these prisms are capped by silicon atoms. All of these trigonal prisms are elongated (i.e., stretched along the threefold axes of the prisms), and the fact that these prisms are capped by silicon atoms is in agreement with the waist-contact-restriction rule (13, 25). According to this rule, a central transition metal atom within an elongated trigonal prism of rare earth atoms should not have any rare earth or transition metal neighbors outside the rectangular faces of the trigonal prism. Only the Ni8 and Ni9 atoms have different coordination polyhedra. The Ni9 atoms on the Wyckoff position 2a are again situated in trigonal prisms of neodymium atoms, however, the rectangular faces of these prisms are not capped by silicon, but by neodymium atoms. In this case this is not in violation of the waist-contact-restriction rule, since these trigonal prisms are compressed along the threefold axes and not elongated, as was discussed earlier (13, 25). In addition, the trigonal faces of the prisms around the Ni9 atoms are capped by nickel atoms, thereby increasing the CN of these atoms to 11. The Ni8 atoms on the position 4e have octahedral neodymium coordination. These octahedra are capped above and below by two nickel atoms on the 6_3 axis. The Ni–Si distances cover the relatively narrow range from 230 to 246 pm with an average of 239.8 pm. This distance is smaller than the sum of the CN 12 radii of 256.5 pm (24) and close to the sum of the single-bond radii of 232.7 pm given by Pauling (26). Most Ni–Ni distances are greater than 400 pm and therefore nonbonding. The only exceptions are the Ni8–Ni9 and Ni8–Ni8 distances of 277 and 282 pm, respectively.

The silicon atoms are also situated in trigonal prisms formed by neodymium atoms. These trigonal prisms are again augmented by three atoms outside the rectangular faces of the prisms: 3Ni, or 2Ni plus 1Nd, or 1Ni plus 2Nd. Thus, there are no Si–Si interactions. The shortest Si–Si distance is 405 pm.

The coordination polyhedra in the structure of $Nd_6Ni_{2-x}Si_3$ (Table 2 and Fig. 4) are all also found in $Nd_{42}Ni_{22-x}Si_{31}$ and show the same tendencies in their bond lengths.

Both structure refinements resulted in very similar occupancy values for the two nickel sites on the 6_3 axes of the two structures. As was already discussed above, a full occupancy of these two sites is not possible for steric reasons. We have placed nickel atoms on these partially occupied sites for various reasons. First of all, a refinement with partial occupancy solely by silicon atoms could be ruled out, because it resulted in occupancy values higher than what is possible for steric reasons. A mixed occupancy was also

TABLE 3
Interatomic Distances in the Structure of $Nd_{42}Ni_{22.67(2)}Si_{31}$[a]

Nd1: 1Ni9 280.8	2Nd3 378.7	2Nd7 417.9	1Si2 316.1	2Nd5 397.9	2Nd10 314.8	Si5: 1Ni3 238.4
2Ni8 288.9	1Nd7 382.4	Nd8: 1Ni4 292.8	2Ni2 317.6	2Nd14 402.0	Ni7: 1Si8 241.4	1Ni5 240.1
2Si4 300.9	1Nd1 404.9	1Si7 293.8	2Si3 319.6	2Nd14 417.9	2Si7 243.8	2Nd6 304.2
1Si4 309.0	1Nd9 407.0	2Ni7 295.8	1Si10 320.8	Ni1: 1Si6 235.1	1Nd13 280.7	2Nd3 304.5
2Ni8 314.3	2Nd4 417.9	2Si8 301.8	1Nd9 383.2	1Si3 237.5	2Nd8 295.8	2Nd7 317.7
2Ni9 350.0	Nd5: 1Ni2 294.7	2Si9 305.8	1Nd12 385.0	1Si1 242.6	1Nd14 315.6	1Nd9 333.5
4Nd1 350.0	1Ni4 294.8	2Nd12 371.8	2Nd2 387.9	2Nd9 293.9	2Nd10 321.3	Si6: 1Ni5 232.0
2Nd4 366.3	2Si9 302.4	1Nd10 381.9	1Nd10 407.6	2Nd11 311.7	Ni8: 1Ni9 276.8	1Ni6 233.4
1Nd4 404.9	2Si10 307.6	2Nd14 386.2	1Nd7 408.6	2Nd7 318.3	1Ni8 282.3	1Ni1 235.1
1Nd3 405.6	1Si7 308.7	1Nd5 395.3	2Nd11 417.9	Ni2: 1Si3 241.0	3Nd1 288.9	2Nd10 313.3
2Nd1 417.9	2Nd13 377.5	1Nd6 399.3	Nd12: 2Ni2 295.0	2Si10 245.6	3Nd1 314.3	2Nd11 314.8
Nd2: 1Ni6 291.2	2Nd12 382.5	2Nd8 417.9	1Si10 299.4	1Nd2 292.5	Ni9: 2Ni8 276.8	2Nd7 315.3
1Ni2 292.5	1Nd8 395.3	Nd9: 2Ni1 293.9	2Si3 303.5	1Nd5 294.7	3Nd1 280.8	Si7: 2Ni7 243.8
2Si10 300.9	2Nd14 397.9	2Si1 304.1	1Si8 338.3	2Nd12 295.0	6Nd1 350.0	1Nd8 293.8
2Si2 305.4	1Nd2 412.4	2Si3 305.9	1Si9 342.8	2Nd11 317.6	Si1: 1Ni3 240.8	2Nd13 304.6
1Si2 326.9	2Nd5 417.9	1Si5 333.5	2Nd8 371.8	Ni3: 1Si5 238.4	1Ni1 242.6	1Nd5 308.7
2Nd2 377.8	Nd6: 2Ni5 298.7	2Nd3 378.9	2Nd5 382.5	1Si1 240.8	2Nd4 303.2	2Nd14 324.2
2Nd13 384.1	2Si5 304.2	2Nd6 380.1	2Nd6 384.9	1Si4 243.9	2Nd9 304.1	Si8: 1Ni5 235.1
2Nd11 387.9	2Si8 306.2	1Nd7 382.8	1Nd11 385.0	2Nd4 291.9	2Nd7 318.0	1Ni7 241.4
1Nd5 412.4	1Si3 328.0	1Nd11 383.2	1Nd9 411.6	2Nd3 296.2	1Nd3 326.1	2Nd8 301.8
1Nd13 412.8	2Nd9 380.1	1Nd4 407.0	2Nd12 417.9	2Nd7 319.4	Si2: 2Ni6 242.0	2Nd6 306.2
2Nd2 417.9	1Nd7 383.8	1Nd12 411.6	Nd13: 1Ni7 280.7	Ni4: 1Si11 230.4	2Nd2 305.4	2Nd10 312.8
Nd3: 2Ni3 296.2	1Nd10 384.3	2Nd9 417.9	1Ni6 292.6	2Si9 240.3	2Nd13 305.8	1Nd12 338.3
2Si5 304.5	2Nd12 384.9	Nd10: 2Ni5 311.8	2Si7 304.6	1Nd8 292.8	1Nd10 313.0	Si9: 2Ni4 240.3
2Si4 311.2	1Nd8 399.3	2Si8 312.8	2Si2 305.8	1Nd5 294.8	Si3: 1Ni1 237.5	2Nd5 302.4
1Si1 326.1	1Nd3 404.6	1Si2 313.0	1Si10 322.5	2Nd14 309.8	1Ni2 241.0	2Nd8 305.8
1Nd4 364.1	2Nd6 417.9	2Si6 313.3	2Nd5 377.5	2Nd14 313.6	2Nd12 303.5	1Nd14 305.9
2Nd4 378.7	Nd7: 2Ni5 312.4	2Ni6 314.8	2Nd10 383.1	Ni5: 1Si6 232.0	2Nd9 305.9	1Nd14 309.7
2Nd9 378.9	2Si6 315.3	2Ni7 321.3	2Nd2 384.1	1Si8 235.1	2Nd11 319.6	1Nd12 342.8
1Nd7 388.6	2Si5 317.7	1Nd8 381.9	1Nd2 412.8	1Si5 240.1	1Nd6 328.0	Si10: 2Ni2 245.6
1Nd6 404.6	2Si1 318.0	2Nd13 383.1	2Nd13 417.9	2Nd6 298.7	Si4: 1Ni3 243.9	1Nd12 299.4
1Nd1 405.6	2Ni1 318.3	1Nd6 384.3	Nd14: 1Si9 305.9	2Nd10 311.8	2Nd1 300.9	2Nd2 300.9
2Nd3 417.9	2Ni3 319.4	1Nd7 404.8	1Si9 309.7	2Nd7 312.4	1Nd1 309.0	2Nd3 311.2
Nd4: 2Ni3 291.9	1Si7 332.5	1Nd11 407.6	2Ni4 309.8	Ni6: 1Si6 233.4	2Nd3 311.2	1Nd11 320.8
2Si1 303.2	1Nd8 382.8	2Nd10 417.9	2Si11 312.3	2Si2 242.0	2Nd4 314.9	1Nd13 322.5
2Si4 314.9	1Nd9 382.8	Nd11: 2Ni1 311.7	2Ni4 313.6	1Nd2 291.2	1Nd4 326.3	Si11: 3Ni4 230.4
1Si4 326.3	1Nd6 383.8	2Ni6 314.6	1Ni7 315.6	1Nd13 292.6		6Nd14 312.3
1Nd3 364.1	1Nd3 388.6	2Si6 314.8	2Si7 324.2	2Nd11 314.6		
2Nd1 366.3	1Nd10 404.8		2Nd8 386.2	2Nd10 314.8		

[a] All distances shorter than 440 (Nd–Nd), 380 (Nd–Ni, Nd–Si, Ni–Si, Si–Si), and 340 pm (Ni–Ni) are listed. Short interatomic distances between the partially occupied Ni8 and Ni9 positions are shown in Fig. 1. Standard deviations are all less than 0.6 pm. Because of the statistical occupancy of the Ni8 and Ni9, positions the Nd1 atoms have Ni8 and Ni9 neighbors at many different distances. In reality, the Nd1 atoms can only have two or three Ni8 and/or Ni9 neighbors. The following three combinations are possible: (a) 2Ni8 at 314.3 pm; (b) 1Ni8 at 288.9 pm and 1Ni9 at 350.0 pm; (c) 2Ni8 at 394.3 pm and 1Ni9 at 280.8 pm.

considered; nevertheless, it resulted in occupancies which consisted mainly of nickel atoms. Furthermore, the shortest interatomic distances of these partially occupied sites to the neodymium atoms (280.8 and 288.9 pm in $Nd_{42}Ni_{22-x}Si_{31}$; 280.6 and 288.8 pm in $Nd_6Ni_{2-x}Si_3$) are very short, as short as the shortest Nd–Ni distance between fully occupied sites (Nd13–Ni7 in $Nd_{42}Ni_{22-x}Si_{31}$: 280.7 pm), and generally the Nd–Ni distances are shorter than the Nd–Si distances, as already discussed. Finally, some further support for the occupancy of the 2a and 4e positions with nickel atoms was provided by the energy-dispersive X-ray fluorescence analysis of the $Nd_6Ni_{2-x}Si_3$ crystals in the scanning electron microscope, which resulted in Ni/Si ratios between 0.31 and 0.90 for six analyses with an average of 0.66. This value is much closer to the value of 0.58, assuming these sites to be occupied by nickel atoms, than the value of 0.27, assuming their occupancy by silicon atoms.

The partial occupancy of the nickel atoms on the 6_3 axes of the two structures is reflected by the displacement parameters of the Nd1 atoms of both structures. These neodymium atoms are adjacent to the partially occupied nickel sites, and it can be assumed that they are located at slightly different positions depending on which of the adjacent nickel sites are occupied. Hence, their displacement
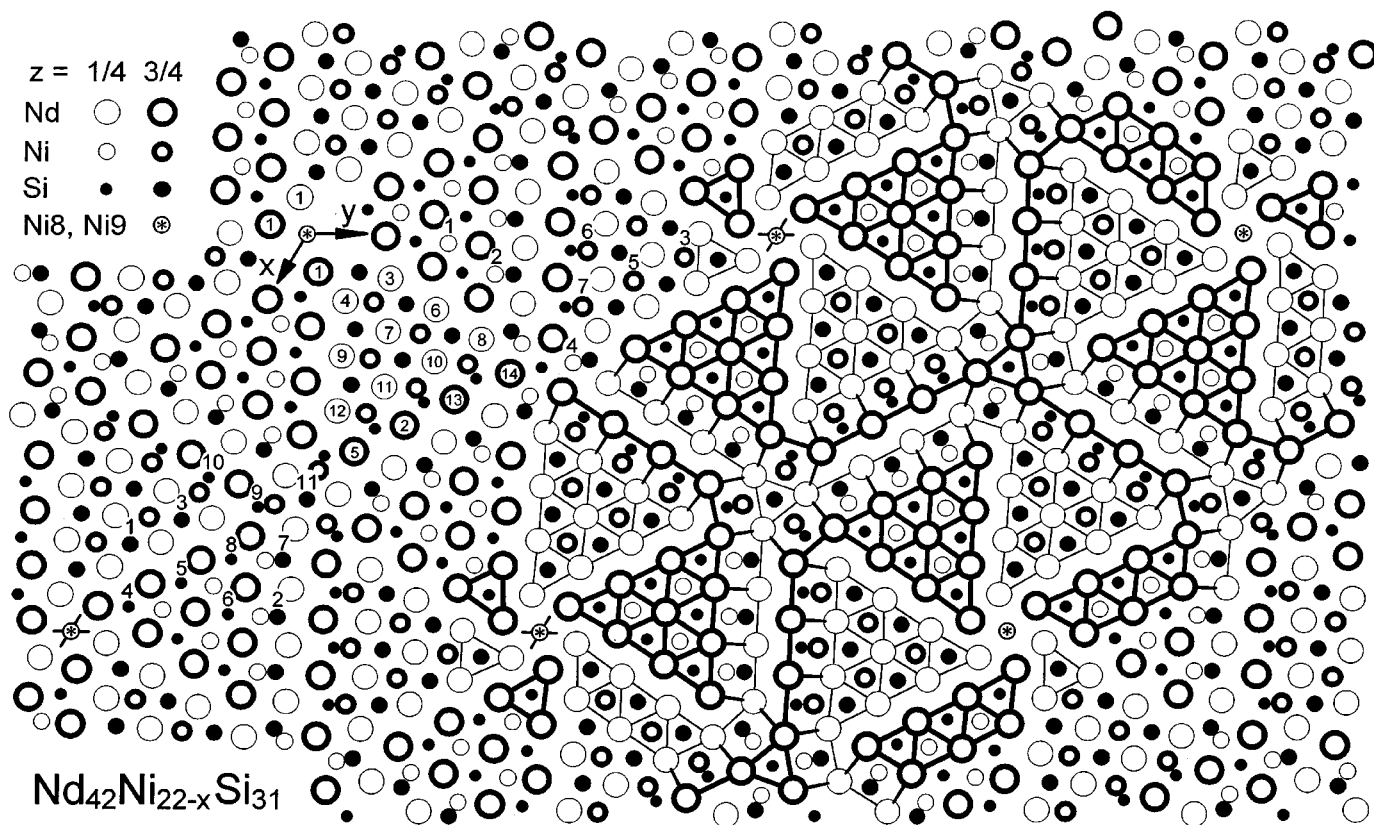
FIG. 2. Projection of the Nd$_{42}$Ni$_{22-x}$Si$_{31}$ structure along the hexagonal axis. The atom designations in the lower left-hand and upper right-hand parts of the outlined cell correspond to the silicon and nickel atoms, respectively. The numbers in the middle part of that cell inside the circles represent the atom designation of the neodymium atoms. In the right-hand part of the figure the trigonal prisms of neodymium atoms surrounding the nickel and silicon atoms are emphasized.

parameters are large, larger than those of any other atom of the two structures.

Our proposal for an ordered distribution of the nickel atoms on the sites 2a and 4e as shown in Fig. 1 could result in superstructure reflections corresponding to a doubling of the c translation period. No such superstructure reflections were observed. Obviously, long-range order would be favored for an occupancy of the 2a and 4e sites with exactly 25%, which is not the case. Also, long-range order in directions perpendicular to the hexagonal axes is difficult to establish, because the translation periods a are rather large. An ordered distribution of the nickel atoms on the sixfold axes with full occupancy of *one* nickel site would be possible for a refinement of the structures in the space group $P\bar{6}$. However, as is frequently the case for hexagonal structures with similar compositions (27), we have not been successful with such refinements. Such refinements always resulted in residual electron densities on the nickel positions corresponding to the position 4e of the space group $P6_3/m$. In a refinement with full occupancy of all atomic positions in the space group $P\bar{6}$, this position must not be occupied.

The structure of Nd$_6$Ni$_{2-x}$Si$_3$ is closely related to the structure of (Mg,Al)$_{12}$Cu$_2$Si$_7$ (28), which has 21 atoms in the hexagonal cell, while Nd$_6$Ni$_{2-x}$Si$_3$ has 21.5. The difference arises mainly through the different occupancies of the sites on the hexagonal axis 0, 0, z; the other atomic sites are practically the same and therefore the two structures may be considered as almost isotypic. The structure of (Mg,Al)$_{12}$Cu$_2$Si$_7$ was actually refined in the space group $P\bar{6}$, although a refinement in $P6_3/m$ was also considered. The same atomic positions as found here for Nd$_6$Ni$_{1.75}$Si$_3$ were also described for the structure of $\sim$Ce$_6$Ni$_2$Si$_3$ (9). The latter structure was refined from single-crystal film data, which did not allow a clear distinction between the nickel and the silicon sites and therefore that structure was reported with mixed Ni/Si occupancy. It seems probable that these two compounds are completely isotypic.

The two compounds Nd$_{42}$Ni$_{22-x}$Si$_{31}$ and Nd$_6$Ni$_{2-x}$Si$_3$ have metal : silicon ratios which are close to the ratio 2 : 1. A large number of silicides, germanides, phosphides, and arsenides have been synthesized in the past 20 years which belong to this extended structural family, of which the Fe$_2$P and TiNiSi type structures are the most simple

TABLE 4
Interatomic Distances in the Structure of $Nd_6Ni_{1.66(1)}Si_3$[a]

Nd1:	1Ni3	280.6		2Nd2	362.7	Ni2:	3Si	242.9
	2Ni1	288.8		2Nd1	368.3		6Nd2	299.0
	2Si	304.1		2Nd2	377.0	Ni3:	[2Ni1	68.4]
	1Si	312.5		1Nd1	398.2		[2Ni1	145.1]
	2Ni1	315.9		1Nd1	398.7		[2Ni3	213.4]
	2Ni3	352.5		2Nd2	426.8		3Nd1	280.6
	4Nd1	352.5	Ni1:	[1Ni3	68.4]		2Ni1	281.8
	2Nd2	368.3		[1Ni1	76.7]		6Nd1	352.5
	1Nd2	398.2		[1Ni1	136.7]	Si:	1Ni2	242.9
	1Nd2	398.7		[1Ni3	145.1]		2Nd1	304.1
	2Nd1	426.8		[2Ni1	213.4]		2Nd2	310.3
Nd2:	2Ni2	299.0		1Ni3	281.8		1Nd1	312.5
	2Si	310.3		3Nd1	288.8		2Nd2	314.4
	2Si	314.4		1Ni1	290.1		1Nd2	327.3
	1Si	327.3		3Nd1	315.9			

[a] All distances shorter than 450 (Nd–Nd), 390 (Nd–Ni, Nd–Si, Ni–Si, Si–Si), and 350 pm (Ni–Ni) are listed. Standard deviations are all less than 0.7 pm. Distances listed in brackets involve partially occupied sites and do not need to occur. Because of the statistical occupancy of the Ni1 and Ni3 positions, the Nd1 atoms have Ni1 and Ni3 neighbors at a variety of distances. The following three combinations are possible: (a) 2Ni1 at 315.9 pm; (b) 1Ni1 at 288.8 pm and 1Ni3 at 352.5 pm; (c) 2Ni1 at 397.6 pm and 1Ni3 at 280.6 pm.

representatives (25, 27, 29–35). In all of these structures the metalloid atoms (Si, Ge, P, As) have trigonal prismatic metal coordination, augmented by three additional metal atoms, which are situated outside the rectangular faces of the prisms as already described. The trigonal axes of these
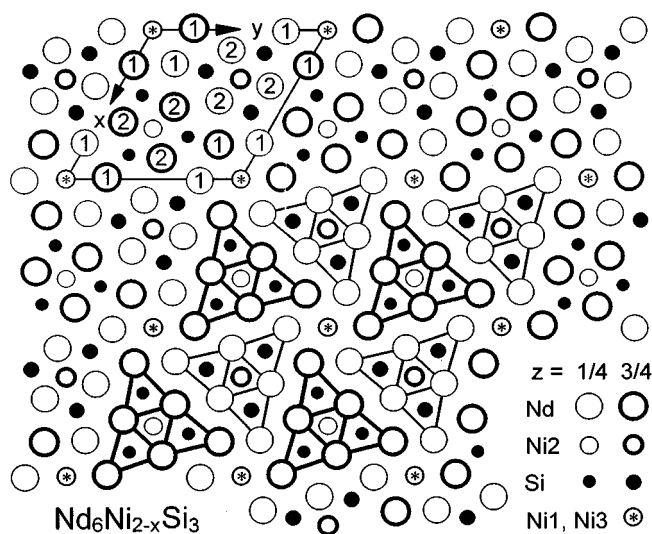

FIG. 4. Coordination polyhedra in the structures of $Nd_{42}Ni_{22-x}Si_{31}$ and $Nd_6Ni_{2-x}Si_3$. All atoms listed in Tables 3 and 4 as neighbors are shown in the coordination polyhedra. There are 10 substantially different coordination shells for the neodymium atoms, which are designated with the letters a–j here and in Table 2. The nickel (k, l, m) and silicon atoms (n, o, p) together have only six different coordination polyhedra. The nickel atoms located on the 6_3 axes are designated with asterisks; two of these partially occupied sites are indicated in the coordination polyhedra a of the Nd1 atoms (cf. Tables 3 and 4).

FIG. 3. Structure of $Nd_6Ni_{2-x}Si_3$ projected along the hexagonal axis. The numbers in the outlined cell correspond to the designations of the neodymium atoms. The trigonal prisms of neodymium atoms containing the nickel and silicon atoms are emphasized in the right-hand part of the figure.
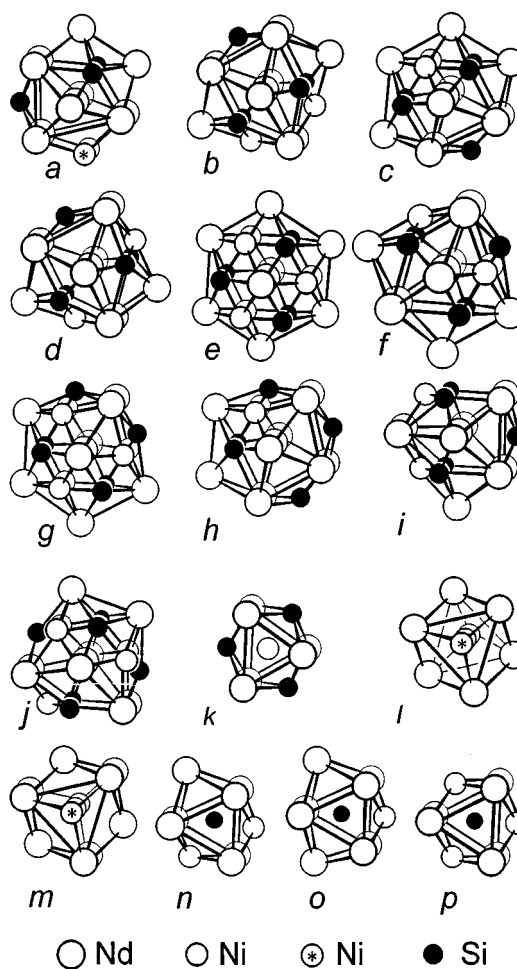
prisms are usually all parallel to the short translation period of these structures. The structure of $Nd_{42}Ni_{22-x}Si_{31}$ is unique in that these trigonal prisms are not only parallel to the (short) hexagonal axis, but some are also aligned perpendicular to this direction.

The structure of $Nd_{42}Ni_{22-x}Si_{31}$ contains building elements, which are outlined in Fig. 5 and also emphasized in Fig. 2. The condensed trigonal prisms as shown in **a** of Fig. 5 were also found in the structure of $Ce_5Ni_2Si_3$ (12–14). The fragment **b** corresponds to the arrangement of trigonal prisms as found in the CrB structure (36). This building element is found in many binary and ternary rare earth transition metal compounds, e.g., TbNi (37, 38), $Pr_{14}Ni_6Si_{11}$
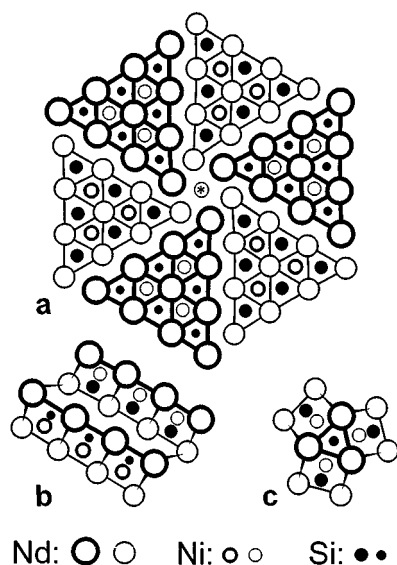
FIG. 5. Three basic building blocks can be visualized in the structure of $Nd_{42}Ni_{22-x}Si_{31}$. The blocks **a** and **b** are found also in other structures of similar compositions. These blocks are projected along the short translation period c and extend indefinitely in this direction.

(29, 39), and $Sm(Pt_{0.53}Ge_{0.47})$ (40). The building element shown in **c** consists of a central elongated neodymium prism, filled with a silicon atom, with condensed prisms attached on each rectangular side of the central prism. These attached prisms are filled alternatingly with nickel and silicon atoms. This building element **c** seems to be novel, occurring for the first time in this structure. In any case, the review article on condensed trigonal prisms by Gladyshevskii and Grin' (41) does not mention this arrangement.

Hexagonal structures sometimes form homologous series with increasing size of the translation period a. Examples are the series $T_{(n+1)(n+2)}M_{n(n+1)+1}$ with the representatives Fe_2P, $Cr_{12}P_7$, and $Rh_{20}Si_{13}$ for $n = 1, 2$, and 3, respectively (30, 31, 42) and $R_{n^2+n}T_{6n^2+6}M_{4n^2+2}$ with UCo_5Si_3 for $n = 2$ (43), $U_6Co_{30}Si_{19}$ for $n = 3$ (44), and $U_{10}Co_{51}Si_{33}$ for $n = 4$ (29, 45). The structure of $Nd_{42}Ni_{22-x}Si_{31}$ ($x = 0.25$) may be considered to be a member of a new homologous series with the general formula $R_{3(n^2+5n+4)}T_{3(n^2+n+2)+2(1-x)}$ $M_{3(n^2+3n+2)+2}$ and $n = 3$. The general formula gives the total cell content $Nd_{84}Ni_{44-2x}Si_{62}$, which corresponds to the more simple formula $Nd_{42}Ni_{22-x}Si_{31}$ with $Z = 2$ formula units per cell. The structures for $n = 1$ ($R_{30}T_{14-2x}M_{20} \Rightarrow$ $R_{15}T_{7-x}M_{10}$) and $n = 2$ ($R_{54}T_{26-2x}Si_{38} \Rightarrow R_{27}T_{13-x}Si_{19}$) are shown in Fig. 6. This series of homologous structures is very similar to the series with the general formula $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ (13, 15, 16) with $Ce_6Ni_2Si_3$ for $n = 2$ (9), $Ce_5Ni_2Si_3$ for $n = 3$ (12), $Pr_{15}Ni_7Si_{10}$ for $n = 4$ (14), and $La_{21}Ni_{11}Si_{15}$ for $n = 5$ (16, 17).

n = 1 $R_{30}T_{14-2x}M_{20} \Rightarrow R_{15}T_{7-x}M_{10}$

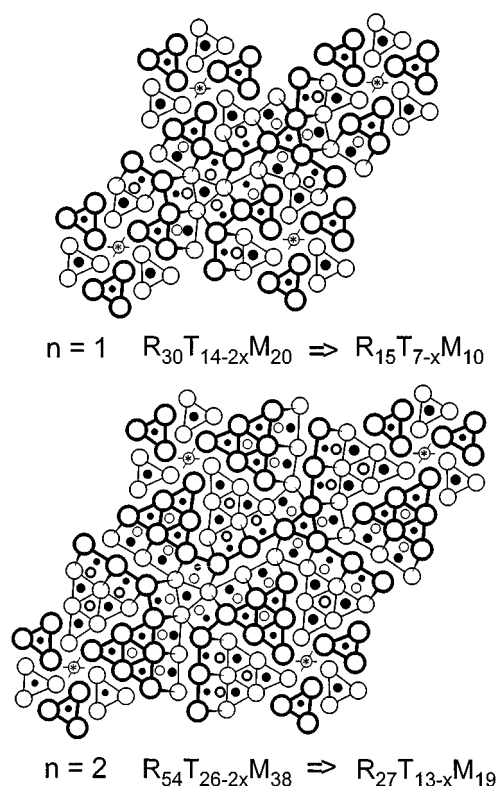n = 2 $R_{54}T_{26-2x}M_{38} \Rightarrow R_{27}T_{13-x}M_{19}$

FIG. 6. The two hypothetical structures with the general formula $R_{3(n^2+5n+4)}T_{3(n^2+n+2)+2(1-x)}M_{3(n^2+3n+2)+2}$, where $n = 1$ and $n = 2$. The two structures are shown in the same way as the structure of $Nd_{84}Ni_{44-2x}Si_{62}$ ($\Rightarrow Nd_{42}Ni_{22-x}Si_{31}$, $Z = 2$, $n = 3$, $x = 0.25$) in Fig. 2.

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