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Pr₁₅Ni₇Si₁₀ with an Atom Ordering on the Trigonal-Prism-Centre Sites in Agreement with the Waist-Contact Restriction Rule

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Abstract. $M_r = 2805.44$, hexagonal, $hP64$, $P6_3/m$, $a = 19.881(1)$, $c = 4.2554(3)$ Å, $V = 1456.7(1)$ Å³, $Z = 2$, $D_x = 6.396$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 292$ cm⁻¹, $F(000) = 2442$, room temperature, final $R = 0.054$ for 876 contributing reflections. The Pr₁₅Ni₇Si₁₀ structure is a member of the structure series Pr _{n^2+3n+2} Ni _{n^2-n+2} Si _{n^2+n} with $n = 4$, characterized by Ni- and Si-centred rare-earth prisms which form trigonal columns, four prisms wide. Where the corners of the trigonal columns meet, a column of face-joined compressed octahedra is formed. The composition of the series and of Pr₁₅Ni₇Si₁₀ corresponds to the case where each octahedral void is occupied by one Ni atom. Pr₁₅Ni₇Si₁₀ has the same structure sites as the earlier reported Pr₁₅Ni₄Si₁₃ (Ce₁₅Ni₄Si₁₃ type) but an ordered arrangement of Ni and Si atoms on the prism-centre sites in agreement with the waist-contact restriction rule.

Introduction. In a recent study on the classification of ternary ordered rare-earth (Y, Sc) (R)–transition-metal (T) silicides and homologues (M), built up of centred trigonal rare-earth prisms, some observations have been made concerning the ordering of the T and M elements on the prism-centre sites (Parthé, Chabot & Hovestreydt, 1983). It was found, that in the case of elongated trigonal prisms (M -centred prisms are always elongated, T -centred prisms are elongated only if they have a common rectangular face with an M -centred

prism) the atom ordering obeys the following restriction rule: Neither R – T nor T – T waist contacts are allowed. This rule has permitted the interpretation of the atomic ordering in Pr₁₄Ni₆Si₁₁ ($mC124$, $C2/m$), Ce₇Ni₂Si₅ ($oP56$, $Pnma$), Gd₃NiSi₂ ($oP24$, $Pnma$) and LaPtSi ($tI12$, $I4,md$), for example. The usefulness of this rule for the understanding of the atom ordering of these compounds led us to reinvestigate the structures of other ternary compounds built up of centred trigonal prisms where no or only partial atom ordering was reported and/or where the waist-contact restriction rule appeared to be violated.

The structures of three hexagonal compounds in the system Ce–Ni–Si can be grouped in the form of a structure series with general formula

$$R_{n^2+3n+2}T_2^{[6,0]}(T,M)_{2n}^{[6,p]}$$

They are Ce₆Ni₂Si₃ ($hP22$, $P6_3/m$) with $n = 2$ (Bodak, Gladyshevskii & Kharchenko, 1974), Ce₅Ni₂Si₃ ($hP40$, $P6_3/m$) with $n = 3$ (Bodak, Gladyshevskii & Mys'kiv, 1972)* and Ce₁₅Ni₄Si₁₃ ($hP64$, $P6_3/m$) with $n = 4$ (Mys'kiv, Bodak & Gladyshevskii, 1974). These structures are characterized by infinite triangular columns, parallel to $\{0001\}$, constructed of face-joined, Ni- and Si-centred, trigonal Ce prisms. The parameter n

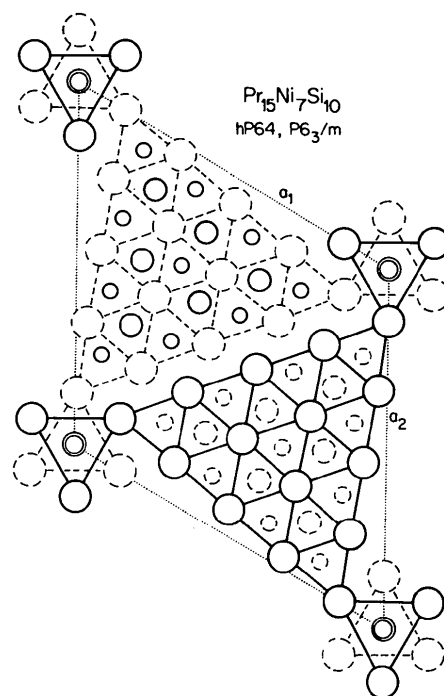
* In the title of the publication the compound is referred to as Ce₂NiSi.

indicates the number of joined trigonal prisms along one of the basal edges of the trigonal columns. At the place where six column corners meet, octahedral voids are formed which are assumed to be occupied each by one Ni atom. The $Ce_{15}Ni_4Si_{13}$ structure with $n = 4$ is shown in Fig. 1(b). Drawings of the other members of this series can be found in Parthé & Chabot (1984). No or only partial atom ordering on the prism-centre sites has been reported for all of these compounds in the original structure papers.

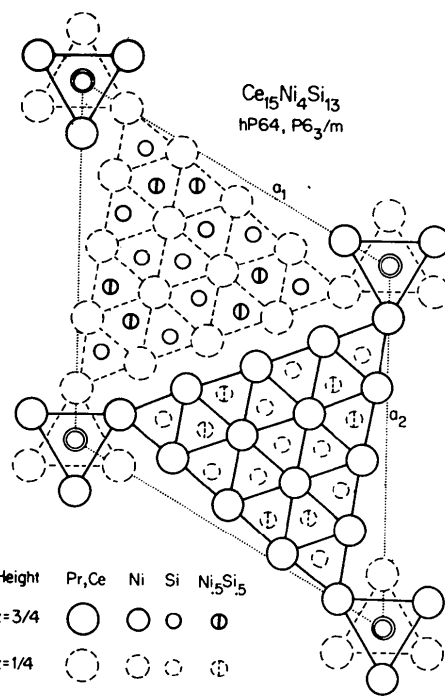
If we consider the arrangement of centred trigonal prisms of reported $Ce_{15}Ni_4Si_{13}$ as shown in Fig. 1(b) and try to position Ni and Si atoms in an ordered fashion on the prism-centre sites such that the number of Ni atoms is the largest possible without Ce–Ni and Ni–Ni waist contacts, we will obtain the atom arrangement shown in Fig. 1(a) with the different composition $Ce_{15}Ni_7Si_{10}$. We found it of interest to study crystal structures of compounds having this calculated composition $R_{15}T_7M_{10}$ and to verify our prediction for atom ordering.

We decided to investigate the atom ordering on the isotypic Pr compound for which Mys'kiv (1973) reported as lattice constants $a = 20.19$ and $c = 4.297$ Å.

Experimental. Compound of nominal composition $Pr_{15}Ni_7Si_{10}$ from ingots of Pr(99.9%), Ni(99.99%) and Si(99.999%) by arc melting under Ar. Wrapped in Ta foil, in quartz tubes under Ar at 1200 K for 12 d. From crushed sample irregular-shaped single crystal with mean diameter 84 μm . Automatic four-circle diffractometer (PW 1100), graphite-monochromated $Mo K\alpha$ radiation. Lattice parameters from 21 reflections ($25 < \theta < 27^\circ$) each centred at 2θ and -2θ . Possible space groups from Weissenberg photographs. Experimental absorption correction ($3.94 < EAC < 6.54$) from 69 reflections, each at 13 different ψ settings (Flack, 1977). $\sin\theta/\lambda < 0.64$ Å $^{-1}$. Intensity variation of standard reflections -511 , 141 and $002 < 2.1\%$. 5479 reflections measured, $0 \leq h, k \leq 21$, $-5 \leq l \leq 5$, all with anti-reflections, $\omega-2\theta$ scan, 1204 unique reflections ($R_{\text{int}} = 0.062$) of which 328 considered unobserved [$I < 1\sigma(I)$] resulting in 876 observed. Pr-atom positions from $Ce_{15}Ni_4Si_{13}$ (Mys'kiv *et al.*, 1974), Ni and Si from difference Fourier map. 56 variables refined using $|F|$ values. $R = 0.054$, $wR = 0.063$, $S = 12.7$, unit weights, final max. Δ/σ 0.00014, residual electron density between -3.43 and 4.08 e Å $^{-3}$. Secondary isotropic extinction correction of type I with a Gaussian distribution (Becker & Coppens, 1974) of 3.9×10^{-6} . Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), lattice-parameter refinement with *FINAX* (Hovestreydt, 1983), all other programs from *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).



(a)



(b)

Height	Pr,Ce	Ni	Si	Ni ₅ Si ₅
$z = 3/4$	○	○	○	⊕
$z = 1/4$	○	○	○	⊕
$z = 0, 1/2$	○	○	○	○

Fig. 1. (a) The fully ordered $Pr_{15}Ni_7Si_{10}$ structure (in agreement with the waist-contact restriction rule) and (b) the reported $Ce_{15}Ni_4Si_{13}$ structure (which violates this rule) in a projection along $[0001]$.

The U_{33} component of the temperature factor of Ni(3) is unusually large, which leads to the high value of U_{eq} . Once the value of 20 Å² (with an e.s.d. of 10) was attained, U_{33} was kept invariant, otherwise the least-squares normal-equation matrix became singular. No diffuse scattering or intermediate reflections, however, could be detected, either on rotation photographs around c or on scans with the automatic single-crystal diffractometer along c^* . As a result, the occupation of the centres of the octahedra is not well defined. It is even not possible to state with precision where the atoms, called here Ni(3), are located along the axis of the octahedral rare-earth columns (coinciding with the c axis). The composition Pr₁₅Ni₇Si₁₀ corresponds to two Ni(3) atoms along the c axis per unit cell which are only 2.13 Å apart. These atoms can probably move more or less freely along the column's axis. Similar anomalies in site occupation and temperature factors for structure sites on the axis of columns of face-joined polyhedra have been observed for example in Y₁₃Pd₄₀Sn₃₁ (Cenzual & Parthé, 1984) and in Y₄Co₃ (Yvon, Braun & Gratz, 1983). It remains to be clarified in a further study if there are defects and/or non-commensurability between the periodicity of the atoms on the column's axis and the translation period of the column itself.

Discussion. Atomic parameters are given in Table 1 and the interatomic distances in Table 2.†

The structure of Pr₁₅Ni₇Si₁₀, presented in Fig. 1(a), obeys the waist-contact restriction rule. The atom ordering of Ni and Si atoms on the prism-centre sites is as predicted. The $R-T$ and $T-T$ waist contacts in the original structure proposal for Ce₁₅Ni₄Si₁₃, shown in Fig. 1(b), do not exist in the fully ordered structure with composition Pr₁₅Ni₇Si₁₀. If a compound has a composition different from the one for perfect order it remains to be clarified if $R-T$ and $T-T$ waist contacts occur at all. The published experimental data for Ce₁₅Ni₄Si₁₃ are inconclusive since the R value of the structure refinement was 0.17. As the compositions for perfect T and M order correspond always to the case where the maximum number of prism-centre sites are occupied by T atoms – under the conditions that there are no $R-T$ and $T-T$ waist contacts – deviations from the ideal composition, ignoring vacancies, appear to be possible only, if at all, by replacing some T atoms by M atoms. It seems unlikely that this deviation from the ideal composition should lead to $R-T$ and $T-T$ waist contacts.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for Pr₁₅Ni₇Si₁₀ with space group $P6_3/m$

U_{eq} is the average of the eigenvalues of U . E.s.d.'s are given in parentheses. The z value of Ni(3) was fixed arbitrarily. No well defined value could be obtained because U_{33} had a value of 20 Å².

		x	y	z	$U_{eq} (\times 100)$
Si(1)	6(h)	0.0609 (6)	0.2559 (6)	0.25	1.1 (2)
Si(2)	6(h)	0.1081 (6)	0.4843 (6)	0.25	1.1 (2)
Pr(1)	6(h)	0.1303 (1)	0.1474 (1)	0.25	1.42 (8)
Ni(1)	6(h)	0.1529 (3)	0.3935 (3)	0.25	1.2 (2)
Ni(2)	6(h)	0.1989 (3)	0.6205 (3)	0.25	1.3 (2)
Si(3)	6(h)	0.2899 (5)	0.4424 (6)	0.25	0.8 (2)
Pr(2)	6(h)	0.3204 (1)	0.1242 (1)	0.25	1.09 (8)
Pr(3)	6(h)	0.3549 (1)	0.3212 (1)	0.25	1.07 (7)
Pr(4)	6(h)	0.5017 (1)	0.0818 (1)	0.25	1.05 (8)
Pr(5)	6(h)	0.5332 (1)	0.2886 (1)	0.25	1.09 (7)
Si(4)	2(c)	0.333	0.667	0.25	1.3 (4)
Ni(3)	2(b)	0	0	0	600 (400)

Table 2. Atomic coordinations with interatomic distances d (Å) (up to $\Delta/\sum r$ of 20%) and $\Delta/\sum r$ (%) for Pr₁₅Ni₇Si₁₀

To indicate the atoms which form the surrounding prism or octahedron and to identify the atoms which are in waist contact with the Ni and Si atoms on the prism-centre sites, all interatomic distances of the Ni and Si atoms are given. In the case of the Pr atoms, however, only non-redundant distances are listed. The atomic radii (r) for Pr, Ni and Si are 1.828, 1.246 and 1.319 Å, respectively (Teatum, Gschneidner & Waber, 1960). $\sum r$ is the sum of radii and $\Delta = d - \sum r$. E.s.d.'s are given in parentheses. Atoms in waist contact with Ni and Si are marked by an asterisk.

	d	$\Delta/\sum r$		d	$\Delta/\sum r$
Ni(1)–Si(2)*	2.38 (2)	–7.2	Si(3)–Ni(2)*	2.38 (1)	–7.2
Si(3)*	2.39 (1)	–6.8	Ni(1)*	2.39 (1)	–6.8
Si(1)*	2.41 (1)	–5.9	2Pr(2)	3.060 (8)	–2.8
2Pr(2)	2.937 (5)	–4.5	2Pr(4)	3.09 (1)	–1.8
2Pr(3)	2.987 (5)	–2.8	2Pr(5)	3.20 (1)	1.6
2Pr(5)	3.241 (4)	5.4	Pr(3)*	3.25 (1)	3.4
Ni(2)–Si(4)*	2.352 (7)	–8.3	Si(4)–3Ni(2)*	2.352 (7)	–8.3
Si(3)*	2.38 (1)	–7.2	6Pr(5)	3.162 (2)	0.5
Si(2)*	2.39 (1)	–6.9	Pr(1)–4Pr(1)	3.498 (3)	–4.3
2Pr(4)	2.953 (4)	–3.9	2Pr(2)	3.683 (3)	0.7
2Pr(5)	3.153 (5)	2.6	Pr(2)	4.028 (4)	10.2
2Pr(5)	3.181 (5)	3.5	Pr(3)	4.055 (3)	10.9
Ni(3)–2Ni(3)	2.1277 (1)	–14.6†	2Pr(1)	4.2554 (3)	16.4
6Pr(1)	2.973 (3)	–3.3	Pr(2)–Pr(3)	3.623 (3)	–0.9
Si(1)–Ni(1)*	2.41 (1)	–5.9	2Pr(3)	3.799 (3)	3.9
2Pr(1)	3.048 (8)	–3.1	Pr(5)	3.841 (2)	5.1
Pr(1)*	3.09 (1)	–1.8	Pr(4)	4.092 (4)	11.9
2Pr(3)	3.12 (1)	–0.8	2Pr(2)	4.2554 (3)	16.4
2Pr(2)	3.16 (1)	0.3	Pr(3)–2Pr(4)	3.799 (3)	3.9
Pr(2)*	3.25 (1)	3.4	Pr(5)	3.911 (4)	7.0
Si(2)–Ni(1)*	2.38 (2)	–7.2	Pr(4)	4.085 (4)	11.7
Ni(2)*	2.39 (1)	–6.9	2Pr(3)	4.2554 (3)	16.4
2Pr(4)	3.07 (1)	–2.4	Pr(4)–Pr(5)	3.791 (3)	3.7
2Pr(3)	3.088 (8)	–1.9	Pr(5)	3.836 (3)	4.9
2Pr(5)	3.19 (1)	1.5	2Pr(4)	3.860 (3)	5.6
Pr(4)*	3.32 (1)	5.7	2Pr(4)	4.2554 (3)	16.4
			Pr(5)–2Pr(5)	4.051 (4)	10.8
			2Pr(5)	4.2554 (3)	16.4

† Assuming Ni(3) is at 000 (and at 00½).

† Lists of structure factors and anisotropic thermal parameters for all atoms in the printed form of the Standard Crystallographic File Structure of Brown (1983) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39893 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

We have shown that the compound with $n = 4$ of the structure series mentioned in the *Introduction* is ordered. If we assume that all compounds of this series are ordered, that all possible prism-centre sites, which are permitted by the waist-contact restriction rule, are occupied by T atoms and all octahedral voids occupied each by one T atom, the formula of the structure series must be written as

$$R_{n^2+3n+2}T_2^{[6,o]}T_{n^2-n}^{[6,p]}M_{n^2+n}^{[6,p]}$$

which gives for $n = 2, 3$ and 4 the compositions $R_6T_2M_3$, $R_5T_2M_3$ and $R_{15}T_7M_{10}$, respectively. We note that for $n = 2$ and 3 the calculated compositions agree with those previously reported, although no complete ordering was found. Experiments are presently being undertaken to find out if these compounds are not perhaps ordered after all.

We have demonstrated here how the waist-contact restriction rule can be used to find the correct composition for perfect order of a structure, built up of centred trigonal prisms where only the structure sites are known with certainty. The predicted change from $\text{Pr}_{15}\text{Ni}_4\text{Si}_{13}$ to $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$ represents the second successful application of the waist-contact restriction rule, which led to the prediction of a change of composition of a ternary rare-earth-nickel silicide. From the arrangement of the centred trigonal prisms in $\text{Ce}_{14}\text{Ni}_8\text{Si}_9$ (Mys'kiv, 1973) it was possible to conclude that the composition for perfect order should be $\text{Ce}_{14}\text{Ni}_6\text{Si}_{11}$ (Parthé *et al.*, 1983), which was experimentally verified by Hovestreydt (1984). A further experiment is being undertaken to verify if $\text{Ce}_{15}\text{Ni}_7\text{Si}_{10}$ also crystallizes with the ordered $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$ type.

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Cubic $\text{Sc}_{57}\text{Rh}_{13}$ and Orthorhombic $\text{Hf}_{54}\text{Os}_{17}$, Two Geometrically Related Crystal Structures with Rhodium- and Osmium-Centred Icosahedra

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Abstract. $\text{Sc}_{57}\text{Rh}_{13}$: $M_r = 3900.3$, $cP140$, $Pm\bar{3}$, $a = 14.4051(7) \text{ \AA}$, $V = 2989.1(2) \text{ \AA}^3$, $Z = 2$, $D_x = 4.33 \text{ g cm}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.7107 \text{ \AA}$, $\mu = 93.4 \text{ cm}^{-1}$, $F(000) = 3564$, $T = 293 \text{ K}$, $wR = 0.051$ for 1013 independent reflections. Isotypic compounds are $\text{Sc}_{57}\text{Ru}_{13}$ [$a = 14.394(1) \text{ \AA}$], $\text{Sc}_{57}\text{Ir}_{13}$ [$a = 14.364(1) \text{ \AA}$] and $\text{Sc}_{57}\text{Pt}_{13}$ [$a = 14.415(1) \text{ \AA}$]. $\text{Hf}_{54}\text{Os}_{17}$: $M_r = 12871.9$, $oI142$, $Immm$, $a =$

$13.856(2)$, $b = 14.104(2)$, $c = 14.570(2) \text{ \AA}$, $V = 2847.2(6) \text{ \AA}^3$, $Z = 2$, $D_x = 15.0 \text{ g cm}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.7107 \text{ \AA}$, $\mu = 1433 \text{ cm}^{-1}$, $F(000) = 10360$, $T = 293 \text{ K}$, $R = 0.084$ for 1057 independent reflections. The $\text{Sc}_{57}\text{Rh}_{13}$ and $\text{Hf}_{54}\text{Os}_{17}$ structures can be considered as slight deformations of a hypothetical cubic, body-centred structure type built up from icosahedra centred by the minority atoms. In the structural unit 12

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