

Discussion. Final positional and isotropic temperature factors are given in Table 1.* Bond lengths associated with the different polyhedra are given in Table 2.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38283 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic thermal parameters*

	Occupancy	x	y'	z	B(Å ²)
M(0)	0.62 K + 0.14Na + 0.14Ba + 0.10Sr	0	0	0	1.24 (6)
M(1)	0.7 Zr + 0.3 Ca	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.26 (3)
M(2)	0.9 Mg + 0.9 Fe	0.3111 (1)	0.3111 (1)	0.3111 (1)	0.36 (5)
M(3)	0.9 Ti + 3.1 Cr + 1.3 Fe + 0.7 (V,Nb,Mg)	0.3479 (2)	0.1227 (2)	0.0232 (2)	0.58 (2)
M(4)	6 Ti	0.3071 (2)	0.7208 (2)	0.1457 (2)	0.38 (2)
M(5)	6 Ti	0.4754 (2)	0.0832 (2)	0.6386 (2)	0.38 (2)
M(6)	0.2 Mg	0.3692 (26)	0.3692 (26)	0.3692 (26)	2.23 (1.19)
O(1)		0.3084 (7)	0.6261 (7)	0.3820 (7)	0.52 (9)
O(2)		0.1553 (7)	0.2394 (7)	0.9392 (6)	0.52 (9)
O(3)		0.9218 (7)	0.4583 (7)	0.2979 (7)	0.52 (8)
O(4)		0.1424 (7)	0.5175 (7)	0.9902 (7)	0.52 (8)
O(5)		0.3901 (7)	0.4879 (7)	0.1343 (7)	0.37 (8)
O(6)		0.7043 (6)	0.2434 (7)	0.0743 (7)	0.42 (8)
O(7)	PP = 1.056 (18)	0.2133 (3)	0.2133 (3)	0.2133 (3)	0.45 (14)

Table 2. *M—O bond lengths (Å)*

M(0) cuboctahedron	M(4) octahedron (titanium)
M(0)—O(2) × 6	M(4)—O(2)
M(0)—O(6) × 6	M(4)—O(6)
Mean	M(4)—O(3)
	M(4)—O(5)
M(1) octahedron	M(4)—O(1)
M(1)—O(1) × 6	M(4)—O(6)'
	Mean
M(2) tetrahedron	M(5) octahedron (titanium)
M(2)—O(5) × 3	M(5)—O(4)
M(2)—O(7)	M(5)—O(1)
Mean	M(5)—O(3)
	M(5)—O(5)
M(3) octahedron	M(5)—O(6)
M(3)—O(4)	M(5)—O(5)'
M(3)—O(3)	Mean
M(3)—O(2)	
M(3)—O(4)'	M(6) octahedron
M(3)—O(7)	M(6)—O(5) × 3
M(3)—O(2)'	M(6)—O(1) + 3
Mean	Mean

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Tetradecapraseodymium Hexanickel Undecasilicide, Pr₁₄Ni₆Si₁₁, with Centered Trigonal Rare-Earth Prisms

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Abstract. $M_r = 2634$, monoclinic, $C2/m$, $a = 113.72(1)^\circ$, $V = 2809.7 \text{ \AA}^3$, $Z = 4$, $D_x = 33.991(3)$, $b = 4.2328(4)$, $c = 21.330(3) \text{ \AA}$, $\beta = 6.226 \text{ Mg m}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.71069 \text{ \AA}$, $\mu =$

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27.99 mm⁻¹, $F(000) = 4592$, $T = 293$ K, $R = 0.072$ for 2540 independent reflections. The structure consists of an arrangement of Ni- and Si-centered trigonal prisms of Pr atoms with two mutually perpendicular prism-axis directions. The Ni and Si atoms on the prism-center sites are ordered. A Ni atom has neither a Pr atom nor another Ni atom in prism-waist contact. The Pr₁₄Ni₆Si₁₁ structure is geometrically related to the Ce₁₄(Ni,Si)₁₇ structure. They can be considered as stacking variants of each other.

Introduction. During our efforts to make R_3 NiSi₂ compounds (R = rare-earth element) isotypic with Gd₃NiSi₂ (Klepp & Parthé, 1981), we investigated also the compounds with Pr and found a diffraction pattern different from that of the Gd₃NiSi₂ type. This paper reports on our single-crystal study of the new phase, which was found to have a slightly different composition.

Experimental. Compound of nominal composition Pr₃NiSi₂ prepared by arc melting in an atmosphere of purified argon, starting materials were high-purity elements (Pr 99.9%, Ni 99.99%, Si 99.999%); ingot wrapped in Ta foil, sealed in evacuated silica tube, annealed at 1070 K for two weeks, sample crushed, single crystal of irregular shape, 30 × 60 × 100 μm; automatic four-circle diffractometer (Philips PW 1100), 20 reflections ($42 < 2\theta < 61^\circ$) used for calculating lattice parameters, spherical absorption correction (SAC) applied ($3.88 < SAC < 4.16$, with $\mu R = 1.0$), 3503 reflections measured ($6 < 2\theta < 55^\circ$, $0 < h < 42$, $0 < k < 5$, $-27 < l < 24$), ω - 2θ scan, all unique, 1537 considered observed [$I > 3\sigma(I)$], standard reflections 020, 0 $\bar{2}$ 0 and $\bar{7}$ 15 with a σ of 0.8, 0.8 and 0.6% respectively; direct methods, after the number of reflections with $l = 5n$ (all those with very large E values), used to form the \sum_2 relations, was intentionally limited; Pr positions from an E map, Ni and Si positions from difference Fourier maps, 157 parameters refined using F values of 2540 reflections (1537 observed and 1003 less-thans, calculated greater than observed), isotropic secondary extinction (1×10^{-8}), $R_w = 0.079$ [$w = 1/\sigma^2(F_o)$],* maximum shift/error in final refinement cycle 2.7×10^{-3} ; atomic scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974), structure solved with *SHELXTL* (Sheldrick, 1981), refinement of lattice constants and all other structural parameters with XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Atomic positions and equivalent isotropic temperature factors are listed in Table 1.

* Lists of structure factors and interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38270 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic or equivalent isotropic thermal parameters* ($\text{\AA}^2 \times 10^2$) for Pr₁₄Ni₆Si₁₁ with space group C2/m

The equivalent temperature factors for Pr and Ni are expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$, where U is the mean of the eigenvalues of $U_{\text{anisotropic}}$. E.s.d.'s are given in parentheses. Regardless of the atom species occupying a site, the sites are arranged for each Wyckoff position with increasing x values.

		x	y	z	U
Pr(1)	4(<i>i</i>)	0.0050 (2)	0	0.1827 (3)	1.1 (2)
Ni(1)	4(<i>i</i>)	0.0325 (3)	0	0.4209 (6)	1.3 (4)
Si(1)	4(<i>i</i>)	0.0440 (7)	0	0.621 (1)	0.9 (5)
Si(2)	4(<i>i</i>)	0.0683 (7)	0	0.345 (1)	0.9 (5)
Si(3)	4(<i>i</i>)	0.0741 (7)	0	0.534 (1)	1.3 (5)
Pr(2)	4(<i>i</i>)	0.1059 (1)	0	0.7831 (2)	0.9 (2)
Pr(3)	4(<i>i</i>)	0.1135 (1)	0	0.1461 (3)	0.9 (2)
Ni(2)	4(<i>i</i>)	0.1449 (3)	0	0.3856 (7)	1.2 (4)
Ni(3)	4(<i>i</i>)	0.1501 (3)	0	0.5832 (7)	1.1 (4)
Si(4)	4(<i>i</i>)	0.1812 (6)	0	0.3050 (9)	0.7 (4)
Si(5)	4(<i>i</i>)	0.1850 (8)	0	0.707 (1)	1.7 (5)
Si(6)	4(<i>i</i>)	0.1879 (6)	0	0.5105 (9)	0.2 (4)
Si(7)	4(<i>i</i>)	0.1915 (7)	0	0.111 (1)	1.3 (4)
Pr(4)	4(<i>i</i>)	0.2857 (1)	0	0.3738 (2)	0.9 (1)
Pr(5)	4(<i>i</i>)	0.2889 (1)	0	0.5749 (2)	1.4 (2)
Pr(6)	4(<i>i</i>)	0.2902 (1)	0	0.1765 (2)	0.6 (1)
Ni(4)	4(<i>i</i>)	0.3563 (4)	0	0.1152 (7)	1.4 (4)
Pr(7)	4(<i>i</i>)	0.3857 (1)	0	0.3537 (2)	0.7 (2)
Pr(8)	4(<i>i</i>)	0.3910 (1)	0	0.5375 (3)	1.0 (2)
Si(8)	4(<i>i</i>)	0.4328 (7)	0	0.155 (1)	1.4 (5)
Ni(5)	4(<i>i</i>)	0.4673 (3)	0	0.0793 (6)	1.3 (4)
Pr(9)	4(<i>i</i>)	0.4959 (2)	0	0.3187 (3)	1.2 (2)
Si(9)	4(<i>i</i>)	0.5457 (7)	0	0.125 (1)	1.3 (5)
Si(10)	4(<i>i</i>)	0.5737 (7)	0	0.034 (1)	0.8 (5)
Pr(10)	4(<i>i</i>)	0.6083 (1)	0	0.2838 (2)	0.8 (1)
Ni(6)	4(<i>i</i>)	0.6509 (3)	0	0.0855 (6)	0.8 (4)
Pr(11)	4(<i>i</i>)	0.7107 (1)	0	0.2280 (2)	0.9 (1)
Pr(12)	4(<i>i</i>)	0.7117 (1)	0	0.0233 (2)	0.8 (1)
Si(11)	4(<i>i</i>)	0.8142 (7)	0	0.089 (1)	1.5 (4)
Pr(13)	4(<i>i</i>)	0.8914 (1)	0	0.0377 (3)	0.9 (2)
Pr(14)	2(<i>d</i>)	0	0.5	0.5	1.0 (3)
Pr(15)	2(<i>a</i>)	0	0	0	0.8 (2)

The structure of Pr₁₄Ni₆Si₁₁ is shown on the left-hand side of Fig. 1 in a projection along the short b axis. All Pr atoms participate in the formation of trigonal prisms which are centered by Ni or Si atoms.

Structures built up only with centered trigonal prisms can be classified according to:

(a) the number of different prism-axis directions (Parthé & Chabot, 1983);

(b) the value of the trigonal-prism linkage coefficient LC (Parthé & Moreau, 1977; Parthé, 1981);

(c) the number of intergrown centered trigonal prisms and number of intergrown empty segments of the W-type structure (Grin', Yarmolyuk & Gladyshevskii, 1979; Gladyshevskii & Grin', 1981).

In Pr₁₄Ni₆Si₁₁ all prism axes have only two mutually perpendicular directions (either parallel to \mathbf{b} or parallel to \mathbf{c}). Thus this structure belongs, according to the classification of Parthé & Chabot (1983), to subdivision IIa.

The linkage coefficient LC denotes the average number of centered prisms in which the rare-earth atoms participate. LC corresponds to six times the ratio of the number of trigonal prisms to the number of rare-earth atoms in one unit cell. The composition of the compound is directly related with the LC value according to R_6X_{LC} , where R indicates the rare-earth

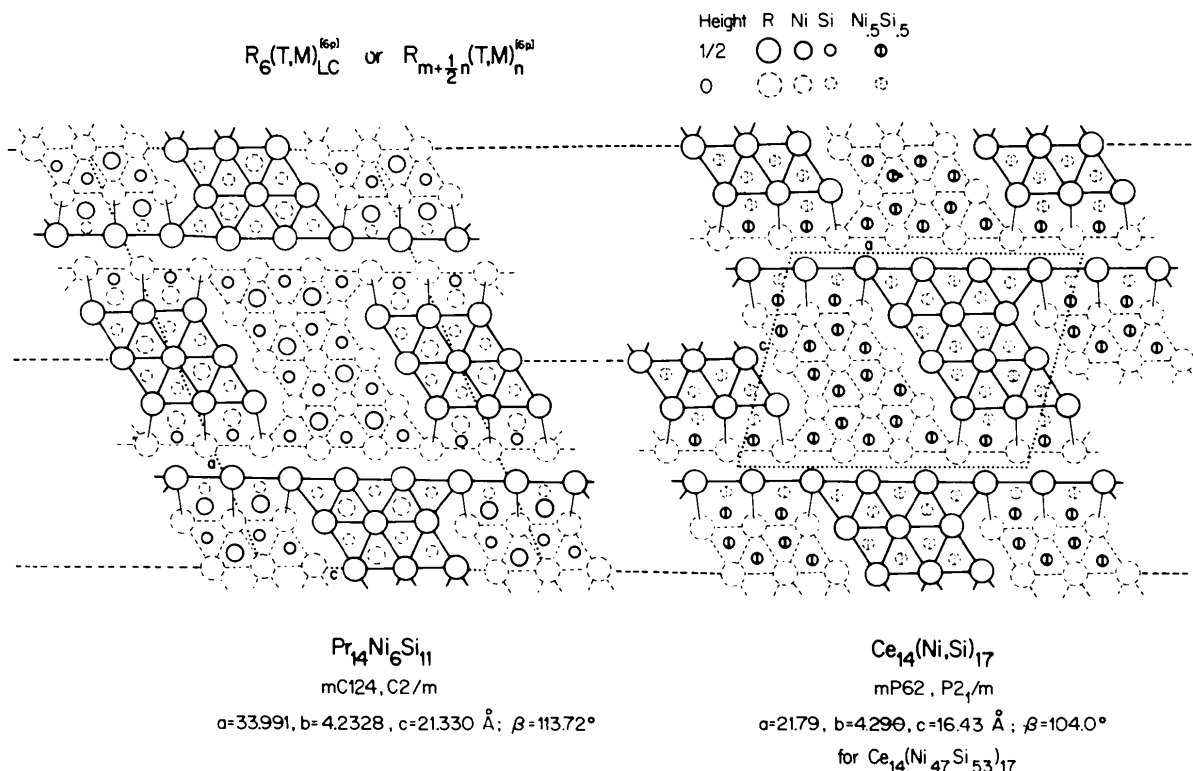


Fig. 1. The Pr₁₄Ni₆Si₁₁ and the Ce₁₄(Ni,Si)₁₇ structures which are related as stacking variants. Both are built up only from centered trigonal rare-earth prisms with LC = 7 $\frac{2}{7}$ and only two perpendicular prism-axis directions. The Ce₁₄(Ni,Si)₁₇ structure is obtained from the Pr₁₄Ni₆Si₁₁ structure if the upper half of the drawing is shifted along the dashed line to the right for $\frac{1}{2}c$ and out of the plane of projection for $\frac{1}{2}b$.

atoms and X the atoms in the prism centers. For Pr₁₄Ni₆Si₁₁ the LC value is 7 $\frac{2}{7}$.

If the space between the blocks of centered rare-earth prisms is also considered, the structure can be thought of as an intergrowth of centered prisms with empty segments of W type built up of rare-earth atoms. The segments are defined in such a way that one unit cell of W contains two such segments. The number of W -type segments in one unit cell is m and the number of centered trigonal prisms is n . The ratio $\frac{m}{n}$ is related to LC according to

$$\frac{m}{n} = \frac{6}{LC} - \frac{1}{2} \quad (1)$$

and the composition of the compound can thus be written $R_{(m/n)+\frac{1}{2}}X$. In the particular case of Pr₁₄Ni₆Si₁₁, one obtains from (1) that $\frac{m}{n} = \frac{11}{34}$. A study of the drawing of Pr₁₄Ni₆Si₁₁ reveals that there are in one unit cell 22 W -type segments and 68 centered prisms.

The Ni and Si atoms on the prism-center sites are ordered. It is found that a Ni atom has neither a Pr atom nor another Ni atom in prism-waist contact, while short Si-Si and Ni-Si distances can occur [2.46 (4) and 2.25 (2) Å respectively]. This rule for ordering is also observed with other ordered ternary rare-earth-

transition-metal silicides and germanides (Parthé, Chabot & Hovestreydt, 1983).

On the right-hand side of Fig. 1 is shown, in a projection along the short b axis, the structure of monoclinic primitive Ce₁₄(Ni,Si)₁₇, determined by Mis'kiv (1973). Pr₁₄Ni₆Si₁₁ and Ce₁₄(Ni,Si)₁₇ can be considered stacking variants of each other. If the upper half of the Pr₁₄Ni₆Si₁₁ structure is shifted along the dashed line for $\frac{1}{2}c$ and out of the plane of projection for $\frac{1}{2}b$ the Ce₁₄(Ni,Si)₁₇ structure is obtained, except for the order of the Ni and Si atoms. Ce₁₄(Ni,Si)₁₇ has a unit cell only half as large as that of Pr₁₄Ni₆Si₁₁. There are also only two mutually perpendicular prism-axis directions. Since the compositions are the same we also find here LC = 7 $\frac{2}{7}$ and $\frac{m}{n} = \frac{11}{34}$; however, there are only 11 W -type segments and 34 centered prisms per unit cell. It can be expected that at composition Ce₁₄Ni₆Si₁₁ an ordered atom arrangement will be found.

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Tétrafluorure de Neptunium Hydraté, $\text{Np}_3\text{F}_{12}\cdot\text{H}_2\text{O}$

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Abstract. $M_r = 957$, triclinic, $P1$, $a = 8.455(8)$, $b = 8.858(9)$, $c = 8.396(10)$ Å, $\alpha = 113.83$, $\beta = 116.64$, $\gamma = 58.03^\circ$, $Z = 2$, $V = 465.2$ Å³, $D_x = 6.83$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 774$, $R(F) = 0.079$, $R_w = 0.104$ for 2848 independent reflexions. Three kinds of F polyhedra surrounding Np are linked in a three-dimensional framework. Np–F distances vary between 2.18 (3) and 2.78 (4) Å; the shortest F–F is 2.44 (7) Å. Water molecules are located in the holes, respectively at 2.54 (13) and 2.43 (10) Å from Np atoms.

Introduction. L'étude par synthèse hydrothermale des systèmes $\text{NaF}-\text{AF}_4$ ($A = \text{U}, \text{Np}$) a permis de mettre en évidence une variété de tétrafluorure de neptunium hydraté. L'état de charge du neptunium a été confirmé par spectroscopie Mössbauer de ²³⁷Np, qui indique par ailleurs l'existence d'un gradient de champ électrique important. Comme pour les autres complexes fluorés de neptunium tétravalent, le gradient de champ électrique suggérait une répartition dissymétrique des charges entourant l'atome de neptunium. Nous avons entrepris l'étude structurale de ce composé afin de déterminer d'une part sa formule chimique exacte et de vérifier d'autre part que l'éclatement quadrupolaire observé par résonance Mössbauer est bien dû essentiellement à une contribution du réseau cristallin.

Des monocristaux de cette nouvelle phase ont été isolés en très faible quantité au cours de l'étude des systèmes $\text{NaF}-\text{AF}_4$ ($A = \text{U}, \text{Np}$). Il est également possible de les préparer sans fluorure alcalin en présence d'acide fluorhydrique à partir soit du dioxyde de neptunium soit du tétrafluorure de neptunium (HF à 40%, $P \simeq 200$ MPa, $T \simeq 600$ K).

Partie expérimentale. Le monocristal étudié a été assimilé à une sphère de rayon égal à 200 µm; l'étude a été conduite à partir de données recueillies sur un diffractomètre automatique Nonius CAD-4 muni d'un monochromateur en graphite; les paramètres réticulaires ont été affinés à l'aide de 17 réflexions; les conditions de mesures étaient les suivantes: radiation $\text{Mo } K\alpha$, $\theta_{\text{max}} = 30^\circ$, $h_{\text{max}} = 11$, $k_{\text{max}} = 12$, $l_{\text{max}} = 11$, balayage $\omega-2\theta$, angle de balayage $(0,80 + 0,35 \text{ tg } \theta)^\circ$, une demi-sphère mesurée; un contrôle en intensité était effectué toutes les heures et un contrôle en orientation après chaque mesure de cent réflexions; 2848 réflexions non nulles (23 sous fond) ont été enregistrées dans ces conditions et corrigées des facteurs de Lorentz–polarisation; on a effectué des corrections d'absorption sphérique ($\mu R = 2,7$); $R_{\text{int}} = 0,03$; l'étude de la fonction de Patterson tridimensionnelle a permis de localiser les atomes lourds; après une première série d'affinements par moindres carrés en $P1$ qui corrige successivement le