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Hexapraseodymium Heptanickel Tetrasilicide, $Pr_6Ni_7Si_4$, an Intergrowth of $ThSi_2$- and $Y_3Rh_2Si_2$-Type Slabs

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Abstract. $M_r = 1368.76$, $oP68$, orthorhombic, *Pbcm*, $a = 5.888$ (1), $b = 7.4265$ (9), $c = 29.558$ (8) Å, $V = 1292.6$ (2) Å³, $Z = 4$, $D_x = 7.033$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 32.24$ mm⁻¹, $F(000) = 2424$, room temperature, final $R = 0.026$ for 1011 contributing reflections. The $Pr_6Ni_7Si_4$ structure can be considered as an intergrowth of $ThSi_2$- and $Y_3Rh_2Si_2$-type slabs. It is built up exclusively of trigonal prisms formed by Pr atoms and centered by Ni or Si atoms. Apart from the central part of the $ThSi_2$ slab, the structure obeys the waist-contact restriction rule. $Ce_6Ni_7Si_4$ [$a = 5.942$ (2), $b = 7.438$ (2), $c = 29.24$ (1) Å], and $Nd_6Ni_7Si_4$ [$a = 5.819$ (2), $b = 7.414$ (3), $c = 29.66$ (1) Å] are isotypic with $Pr_6Ni_7Si_4$.

Introduction. Systems of rare-earth element–transition element–silicon are characterized by an unusually large number of ternary compounds (Parthé & Chabot, 1984). For example, there are 21 known phases of Ce–Ni–Si (Bodak, Mis'kiv, Tyvanchuk, Kharchenko & Gladyshevskii, 1973). Recently, two additional ternary phases were discovered in this system: $Ce_2Ni_3Si_5$ (Chabot & Parthé, 1984) of $U_2Co_3Si_5$ type and $Ce_{14}Ni_6Si_{11}$ (Hovestreydt, 1984) of monoclinic $Pr_{14}Ni_6Si_{11}$ type. Mis'kiv (1973) reported on an unknown orthorhombic phase with approximate composition $Ce_{\sim 10}Ni_{\sim 12}Si_{\sim 3}$ with space group *Pbcm* and lattice constants $a = 5.97$, $b = 7.50$ and $c = 29.2$ Å. An orthorhombic phase with this unit cell was also reported by Bodak, Mis'kiv, Tyvanchuk, Kharchenko & Gladyshevskii (1973), but with approximate composition $Ce_{\sim 8}Ni_{\sim 9}Si_{\sim 3}$. This paper reports on the structure and composition of this compound and other phases isotypic with it.

Table 1. *Atomic positions and thermal parameters* (Å² × 100) *for* $Pr_6Ni_7Si_4$ *with space group Pbcm*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

		x	y	z	U_{eq}
Si(1)	8(e)	0.1111 (7)	0.7299 (5)	0.1734 (1)	1.00 (9)
Pr(1)	8(e)	0.1126 (1)	0.38186 (9)	0.07991 (2)	1.00 (2)
Ni(1)	8(e)	0.1496 (3)	0.0951 (2)	0.01836 (5)	1.19 (4)
Ni(2)	8(e)	0.1611 (3)	0.0289 (2)	0.14775 (5)	1.17 (5)
Si(2)	8(e)	0.3929 (6)	0.0351 (4)	0.0823 (1)	1.01 (9)
Pr(2)	8(e)	0.3948 (1)	0.38797 (9)	0.18110 (2)	1.12 (2)
Ni(3)	8(e)	0.6474 (3)	0.2418 (2)	0.10996 (5)	1.17 (4)
Pr(3)	4(d)	0.1276 (2)	0.0205 (1)	0.25	1.11 (3)
Ni(4)	4(d)	0.6851 (5)	0.1751 (3)	0.25	1.46 (7)
Pr(4)	4(c)	0.6236 (2)	0.25	0	0.97 (3)

Experimental. Preparation of compounds of nominal composition $R_{10}Ni_{12}Si_3$ (R = Ce, Pr, Nd) from R (99.9%), Ni (99.99%) and Si (99.999%) by arc melting under Ar. Wrapped in Ta foil in quartz tubes at 1200 K for 1 d, at 1100 K for 26 d. From crushed sample of Pr alloy prismatic-shaped single crystal, h, l_1, l_2, $l_3 = 80$, 64, 80, 96 µm; automatic four-circle diffractometer (Philips PW 1100); lattice parameters from 28 reflections with $21 < \theta < 27°$; experimental absorption correction ($3.80 < EAC < 5.98$) from 58 reflections, each at 13 different ψ settings (Flack, 1977); $\sin\theta/\lambda < 0.64$ Å⁻¹; standard reflections 029, 506, 130 with intensity variation $<1.5\sigma$; 4294 reflections measured, h, k, l positive up to 7, 9, 37 with antireflections, ω–2θ scan, 1439 unique reflections ($R_{int} = 0.024$), 1011 reflections with $I > 3\sigma(I)$, 428 unobserved; Pr-atom positions from direct methods. Ni and Si from difference Fourier synthesis, composition found to be $Pr_6Ni_7Si_4$; 82 variables refined using F values; R

$= 0.026$, $R_w = 0.029$, $S = 6.02$, unit weights, final max. $\Delta/\sigma = 0.03$, residual electron density between -304 and 320 A s mm^{-3} (-1.9 and 2.0 e Å^{-3}); secondary isotropic extinction correction of type 1 with Gaussian distribution (Becker & Coppens, 1974) of 8.8×10^{-6}; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), all programs from *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic parameters are given in Table 1 and the interatomic distances in Table 2.*

Evaluation of Guinier powder diffraction patterns indicates that Ce$_6$Ni$_7$Si$_4$ and Nd$_6$Ni$_7$Si$_4$ are isotypic with Pr$_6$Ni$_7$Si$_4$. The unit-cell parameters were refined (Cu $K\alpha$, $\lambda = 1.5418$ Å) with *FINAX* (Hovestreydt, 1983), with Si ($a = 5.4308$ Å) as internal standard.

Discussion. A projection of the Pr$_6$Ni$_7$Si$_4$ structure along [100] is shown in Fig. 1. The structure can be considered as an intergrowth of two different kinds of segments. One has the composition $R_3T_4M_2$ (R = rare earth, T = transition element, M = main-group element) and is built up like the ThSi$_2$ type ($tI12$, $I4_1/amd$). In Fig. 2 is presented the LaPtSi type ($tI12$, $I4_1md$), a ternary ordered ThSi$_2$-type derivative (Klepp & Parthé, 1982) in a projection along [110], which allows easy comparison with the structure slab of Pr$_6$Ni$_7$Si$_4$ labelled ThSi$_2$, shown in the top part of Fig. 1. The atom sites in the ThSi$_2$ slab and in the LaPtSi structure are similar; however, the site occupation of the T and M sites is not identical.

The second structure segment in Pr$_6$Ni$_7$Si$_4$ has the composition $R_3T_3M_2$ and is labelled Y$_3$Rh$_2$Si$_2$. A projection of the Y$_3$Rh$_2$Si$_2$ structure, $oP28$, $Pbcm$ (Moreau, Paccard & Paccard, 1984) is shown in Fig. 3. The slab labelled Y$_3$Rh$_2$Si$_2$ has atom sites the same as the corresponding segment in the Y$_3$Rh$_2$Si$_2$ structures; however, M sites are occupied by T atoms and T sites by M atoms. Thus the central part of this slab in Pr$_6$Ni$_7$Si$_4$ consists of linked Pr$_6$Ni prisms in an arrangement identical to Pr$_3$Ni of Fe$_3$C type ($oP16$, $Pnma$).

All Pr atoms in Pr$_6$Ni$_7$Si$_4$ participate in the formation of trigonal prisms that are centered by Ni or Si atoms. However, some of the prisms, particularly those centered by Ni(2), Ni(3), Si(1) and Si(2), are so strongly deformed that they are not easy to recognize. For structures built up exclusively with trigonal prisms the methods of classification have recently been surveyed (Parthé, Chabot & Hovestreydt, 1983). The prism linkage coefficient for Pr$_6$Ni$_7$Si$_4$ is LC = 11. Since

the different prism axes have more than two different directions the Pr$_6$Ni$_7$Si$_4$ structure belongs to class III. For the ordering of T and M atoms on the prism center sites, rules that describe limits on the possible site occupations have been formulated. These rules require, for the case that the prisms are not compressed, that there are (a) no T–R waist contacts and (b) no T–T

Table 2. *Interatomic distances d (Å) (up to $\Delta/\Sigma r$ of 20%) and rounded values of $\Delta/\Sigma r$ (%) for* Pr$_6$Ni$_7$Si$_4$

The atomic radii (r) used for Pr, Ni and Si are 1.828, 1.246 and 1.319 Å, respectively (Teatum, Gschneidner & Waber, 1960). Σr is the sum of radii and $\Delta = d - \Sigma r$. E.s.d.'s are given in parentheses. Atoms in waist contact with Ni or Si at prism centers are marked by an asterisk.

	d	$\Delta/\Sigma r$		d	$\Delta/\Sigma r$
Pr(1)– Ni(2)	2·795 (2)	−9	Ni(1)– Ni(1)*	2·505 (2)	1
Ni(1)	2·810 (2)	−9	Ni(1)*	2·545 (2)	2
Ni(1)	2·863 (2)	−7	Si(2)*	2·413 (4)	−6
Ni(1)	2·918 (2)	−5	Pr(1)	2·810 (2)	−9
Ni(3)	3·062 (2)	0	Pr(1)	2·863 (2)	−7
Ni(3)	3·151 (2)	3	Pr(1)	2·918 (2)	−5
Ni(2)	3·313 (2)	8	Pr(4)	2·940 (2)	−4
Ni(3)	3·433 (2)	12	Pr(4)	3·067 (2)	0
Si(2)	3·060 (4)	−3	Pr(4)	3·348 (2)	9
Si(2)	3·127 (4)	−1	Ni(2)– Ni(3)	2·658 (2)	7
Si(2)	3·187 (4)	1	Si(1)*	2·318 (4)	−10
Si(1)	3·263 (4)	4	Si(1)*	2·365 (4)	−8
Pr(2)	3·422 (1)	−6	Si(2)*	2·368 (4)	−8
Pr(4)	3·851 (1)	5	Pr(1)	2·795 (2)	−9
Pr(4)	3·933 (1)	8	Pr(2)	2·984 (2)	−3
2Pr(1)	3·943 (1)	8	Pr(3)	3·029 (2)	−1
Pr(4)	3·948 (1)	8	Pr(2)	3·159 (2)	3
Pr(2)– Ni(3)	2·795 (2)	−9	Pr(1)	3·313 (2)	8
Ni(2)	2·984 (2)	−3	Pr(2)	3·575 (2)	16
Ni(4)	2·986 (2)	−3	Ni(3)– Ni(2)	2·658 (2)	7
Ni(4)	3·093 (2)	1	Si(2)*	2·296 (4)	−10
Ni(2)	3·159 (2)	3	Si(2)*	2·339 (4)	−9
Ni(3)	3·374 (2)	10	Si(1)*	2·355 (4)	−8
Ni(2)	3·575 (2)	16	Pr(2)	2·795 (2)	−9
Si(1)	3·048 (4)	−3	Pr(1)	3·062 (2)	0
Si(1)	3·145 (4)	0	Pr(1)	3·151 (2)	3
Si(1)	3·210 (4)	2	Pr(4)	3·254 (2)	6
Si(2)	3·359 (4)	7	Pr(2)	3·374 (2)	10
Pr(1)	3·422 (1)	−6	Pr(1)	3·433 (2)	12
Pr(3)	3·609 (1)	−1	Ni(4)–2Si(1)*	2·594 (4)	1
Pr(3)	3·751 (1)	3	Pr(3)	2·792 (3)	−9
Pr(3)	3·818 (1)	4	Pr(3)	2·847 (3)	−7
2Pr(2)	3·914 (1)	7	2Pr(2)	2·986 (2)	−3
Pr(2)	4·073 (2)	11	2Pr(2)	3·093 (2)	1
Pr(3)– Ni(4)	2·792 (3)	−9	Pr(3)	3·477 (3)	13
Ni(4)	2·847 (3)	−7	Si(1)– Ni(2)*	2·318 (4)	−10
2Ni(2)	3·029 (2)	−1	Ni(3)	2·355 (4)	−8
Ni(4)	3·477 (3)	13	Ni(2)*	2·365 (4)	−8
2Si(1)	3·085 (4)	−2	Ni(4)*	2·594 (4)	1
2Si(1)	3·129 (3)	−1	Pr(2)	3·048 (4)	−3
2Pr(2)	3·609 (1)	−1	Pr(3)	3·085 (4)	−2
2Pr(2)	3·751 (1)	3	Pr(3)	3·129 (3)	−1
2Pr(2)	3·818 (1)	4	Pr(2)	3·145 (4)	0
2Pr(3)	4·006 (2)	10	Pr(2)	3·210 (4)	2
Pr(4)–2Ni(1)	2·940 (2)	−4	Pr(1)	3·263 (4)	4
2Ni(1)	3·067 (2)	0	Si(2)– Ni(3)*	2·296 (4)	−10
2Ni(3)	3·254 (2)	6	Ni(3)*	2·339 (4)	−9
2Ni(1)	3·348 (2)	9	Ni(2)	2·368 (4)	−8
2Si(2)	3·211 (4)	2	Ni(1)*	2·413 (4)	−6
2Si(2)	3·226 (3)	3	Pr(1)	3·060 (4)	−3
2Pr(1)	3·851 (1)	5	Pr(1)	3·127 (4)	−1
2Pr(1)	3·933 (1)	8	Pr(1)	3·187 (4)	1
2Pr(1)	3·948 (1)	8	Pr(4)	3·211 (4)	2
2Pr(4)	3·988 (1)	9	Pr(4)	3·226 (3)	3
			Pr(2)	3·359 (4)	7

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39670 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

waist contacts. In the $Pr_6Ni_7Si_4$ structure there are no T–R waist contacts as expected. However, in the $ThSi_2$-type slab there are T–T waist contacts. This is unexpected since the prisms in the $ThSi_2$ type compared, for example, to the prisms in PrNi of CrB type are elongated. We may recall that in PrNi with its compressed prisms ($w/s < 1$) there are T–T waist contacts. The geometry of the $ThSi_2$ types requires, however, that $w/s = 1$. The absence of a compound $PrNi_2$ of the $ThSi_2$ type could be explained by assuming that it violates the T–T waist-contact rule. However, by replacing half of the T atoms with Si atoms in an ordered fashion there are no T–T waist contacts anymore. This is verified by the occurrence of LaPtSi with a $ThSi_2$-type derivative. We tried thus to refine the diffraction data of $Pr_6Ni_7Si_4$ assuming a slightly different composition with Si atoms on some of the Ni sites in the $ThSi_2$-type slabs to avoid T–T waist

contacts [thereby reducing the space-group symmetry from Pbcm to non-centrosymmetric $P22_12_1$ (18), $Pb2_1m$ (26), $P2cm$ (28) or $Pbc2_1$ (29)]. The R value did not change but the structure sites of interest had negative
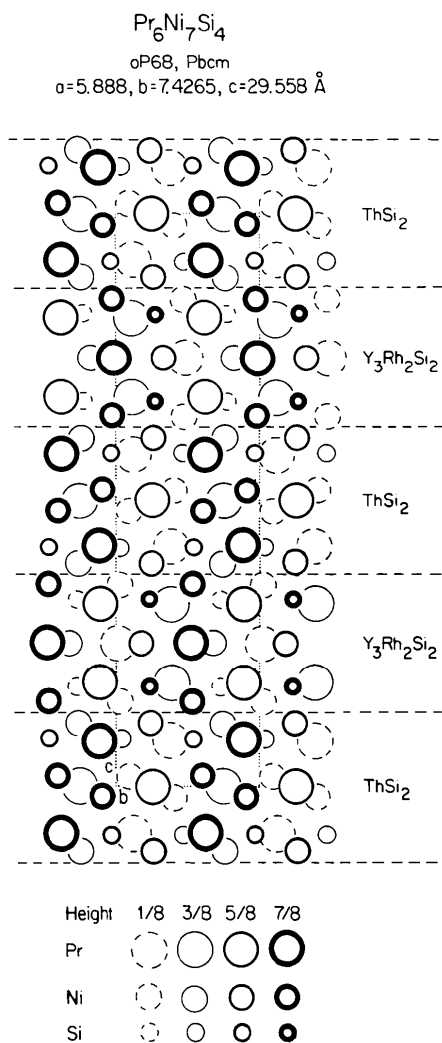
LaPtSi

tI12, I4₁md
a=4.249, c=14.539 Å
projection along [110]
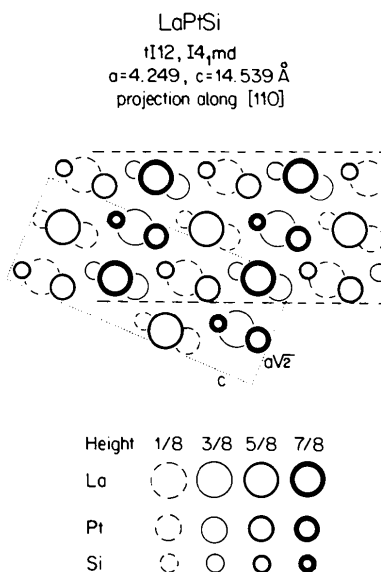

Height   1/8   3/8   5/8   7/8

La

Pt

Si

Fig. 2. Projection of the LaPtSi structure, a ternary ordered $ThSi_2$-type derivative, in a projection along [110]. The slab indicated here by dashed lines corresponds to the uppermost slab in $Pr_6Ni_7Si_4$ (Fig. 1).

$Pr_6Ni_7Si_4$

oP68, Pbcm
a=5.888, b=7.4265, c=29.558 Å

$ThSi_2$

$Y_3Rh_2Si_2$

$ThSi_2$

$Y_3Rh_2Si_2$

$ThSi_2$

Height   1/8   3/8   5/8   7/8

Pr

Ni

Si

Fig. 1. Projection of the $Pr_6Ni_7Si_4$ structure along [100].

$Y_3Rh_2Si_2$

oP28, Pbcm
a=5.566, b=7.717, c=13.043 Å

Height   1/8   3/8   5/8   7/8

Y

Rh

Si
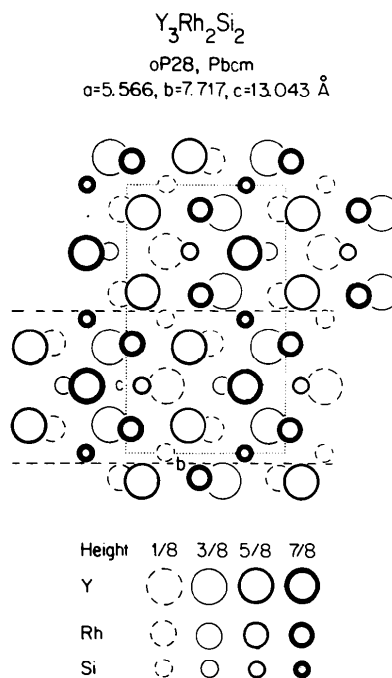
Fig. 3. A projection of the $Y_3Rh_2Si_2$ structure along [100]. The slab in this projection, indicated by dashed lines, corresponds to the second slab from the top in $Pr_6Ni_7Si_4$ (Fig. 1).

temperature factors. It remains to be seen whether or not a sample with composition $R_6T_6M_5$ forms an identical structure but without $T-T$ waist contacts.

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Structural Studies of Thortveitite-Like Dimanganese Diphosphate, Mn₂P₂O₇

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Abstract. $M_r = 283 \cdot 82$, monoclinic, $C2/m$, $a = 6 \cdot 633$ (1), $b = 8 \cdot 584$ (1), $c = 4 \cdot 546$ (1) Å, $\beta = 102 \cdot 67$ (1)°, $V = 252 \cdot 6$ (1) Å³, $Z = 2$, $D_x = 3 \cdot 732$ (1) Mg m⁻³, $F(000) = 272$, $T = 295$ K. X-ray powder diffraction data (Cr $K\alpha_1$, $\lambda = 2 \cdot 28975$ Å, $R = 0 \cdot 083$ for 35 reflections), X-ray single-crystal data (Mo $K\alpha$, $\lambda = 0 \cdot 7107$ Å, $\mu = 5 \cdot 86$ mm⁻¹, $R = 0 \cdot 040$ for 672 reflections), and neutron powder diffraction ($\lambda = 1 \cdot 8820$ Å, $R_I = 0 \cdot 051$ for 50 reflections). Isomorphism with thortveitite, $Sc_2Si_2O_7$, is confirmed, but the refinements, using both a linear and a split-atom model, indicate a disordered bridging oxygen in the diphosphate anion with a non-linear P—O—P bond of $165 \cdot 9$ (1)°. The metal–oxygen distances conform with those of similar compounds. The JCPDS Diffraction File No. is 35-1497 for Mn₂P₂O₇.

Introduction. Among the condensed diphosphates there are often groups of isomorphous compounds, *e.g.* many divalent-metal $M_2P_2O_7$ diphosphates crystallize with the thortveitite-type structure. The crystal structure of thortveitite, $(Sc,Y)_2Si_2O_7$, was originally determined by Zachariasen (1930). The space-group symmetry was reported as $C2/m$, which implies a linear Si—O—Si bond in the disilicate anion. The metal ions are octahedrally coordinated. Since then many studies of thortveitite-type $M_2X_2O_7$ compounds ($X = $ Si, P, V or As) have been published, which have in common the peculiarities that the bridging oxygen has a very large thermal motion, and the XO_4 tetrahedra are more regular than they should be, considering that they share corners with each other (*cf.* Cruickshank, 1961). The possibilities of a lower space-group symmetry or structural disorder have been considered by many authors, although with no definite results (*e.g.* Cruickshank, Lynton & Barclay, 1962; Dorm & Marinder, 1967; Robertson & Calvo, 1968).

We now report on some crystallographic studies of Mn₂P₂O₇. This compound is the only diphosphate known to possess the thortveitite structure at room temperature. Crystallographic investigations of this phase have been undertaken earlier, although with less accurate data, giving R factors of $0 \cdot 18$ (Lukaszewicz & Smajkiewicz, 1961) and $0 \cdot 12$ (Tondon & Calvo, 1981).