Confirmation of the crystal structure of PrNi$_9$Si$_4$

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The crystal structure of PrNi$_9$Si$_4$ was refined on X-ray single-crystal diffraction data. It was confirmed that the compound crystallizes in the tetragonal system, space group *I*4/*mcm* (a = 7.8335(11), c = 11.466(2) Å, Z = 4; R = 0.0284, wR = 0.0703 for 209 independent reflections and 25 variables). The structure belongs to the structure type CeNi$_{8.5}$Si$_{4.5}$, but shows ordered distribution of the atoms with the Si atoms occupying exclusively one of the sites in Wyckoff position 16*l*.

Praseodymium / Nickel / Silicon / X-ray single crystal diffraction / Crystal structure

Introduction

The interaction of praseodymium with nickel and silicon has not been studied systematically. The existence of 18 ternary compounds has been reported in the Pr–Ni–Si system [1-3] (Table 1). The crystal structures of the following compounds have been refined on X-ray diffraction data: PrNi$_9$Si$_4$ (powder), PrNi$_2$Si$_2$ (single-crystal, powder), PrNiSi$_2$ (powder), Pr$_6$Ni$_7$Si$_4$ (single-crystal), Pr$_3$NiSi$_3$ (powder), Pr$_{14}$Ni$_6$Si$_{11}$ (single-crystal), Pr$_{15}$Ni$_7$Si$_{10}$ (single-crystal), Pr$_5$Ni$_{1.9}$Si$_3$ (single-crystal; Pr$_5$Ni$_2$Si$_3$: powder), Pr$_6$Ni$_{1.76}$Si$_3$ (single-crystal; Pr$_6$Ni$_{1.57}$Si$_3$: powder). The structure of PrNi$_{0.5}$Si$_{1.5}$ has fixed coordinates for all the atoms.

In 1969, Bodak and Gladyshevskii [4] reported that the ternary systems R–Ni–Si (R = La, Ce, Pr, Nd, Sm, and Eu) contain a ternary compound of composition ~RNi$_{8.5}$Si$_{4.5}$ with a tetragonal structure closely related to the cubic NaZn$_{13}$-type [5]. These compounds show limited homogeneity ranges along the isoconcentrate 7.14 at.% R. Ten years later the structure of the compound with Ce was solved from X-ray single-crystal diffraction data: own structure type CeNi$_{8.5}$Si$_{4.5}$, Pearson symbol *tI*56, space group *I*4/*mcm*, a = 7.857, c = 11.503 Å [6]. The Ce atoms were located in Wyckoff position 4*a*, the main part of the Ni atoms in positions 16*l* and 16*k*, and the Si atoms on a second site in Wyckoff position 16*l*. Wyckoff position 4*d* was found to be occupied by a statistical mixture of Ni and Si atoms, for which the

ratio was fixed to 1:1. More recently, similar atom distributions were reported for the compounds with La (a = 7.8723, c = 11.4807 Å) [7], Pr (a = 7.8377, c = 11.4861 Å), Nd (a = 7.836, c = 11.457 Å) [8], and Eu (a = 7.8205, c = 11.525 Å) [9]. However in these cases the composition was RNi$_9$Si$_4$ and the atom distribution fully ordered, Wyckoff position 4*d* being occupied exclusively by Ni atoms.

The aim of the present work was to confirm the ordered atom arrangement in the structure of PrNi$_9$Si$_4$ based on X-ray single-crystal diffraction data.

Experimental

An alloy of nominal composition Pr$_{7.1}$Ni$_{60.8}$Si$_{32.1}$ (PrNi$_{8.5}$Si$_{4.5}$) with a total mass of 2 g was prepared from high-purity elements (Pr: 99.98 wt.%, Ni: 99.99 wt.%, Si: 99.9999 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as getter and a tungsten electrode. To achieve high efficiency of the interaction between the components the sample was melted twice. The composition of the sample was controlled by comparing the mass of the alloy with the total mass of the initial load. The weight loss did not exceed 2 % after melting. The alloy was annealed for two weeks at 600°C under vacuum in a quartz ampoule and subsequently quenched into cold water.

A single crystal, suitable for X-ray investigation, was extracted from the alloy. The first stage of the investigation, by Laue and rotation methods (Mo *K* radiation), indicated tetragonal symmetry and yielded approximate values of the lattice parameters. X-ray diffraction data was collected on a KUMA KM-4 four-circle diffractometer equipped with a CCD detector, using graphite-monochromatized Mo *K*α radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by the Patterson method and refined by the full-matrix least-squares method using the program SHELXL-97 [10]. After the data collection, the single crystal was analyzed by EDX spectroscopy with a Leica420i scanning electron microscope. No impurity elements heavier than sodium were detected. The structure drawings were made with the program ATOMS [11].

Results and discussion

The EDX analysis showed that the composition of the single crystal did not deviate significantly from the stoichiometry PrNi$_9$Si$_4$. The crystal structure of the compound was refined in the space group *I*4/*mcm* and it was confirmed that it belongs to the CeNi$_{8.5}$Si$_{4.5}$ type. Experimental details of the data collection and structure refinement of PrNi$_9$Si$_4$ are presented in

Table 2. Atomic coordinates and displacement parameters for PrNi$_9$Si$_4$ are given in Table 3, whereas interatomic distances, coordination numbers, and coordination polyhedra are listed in Table 4. Like the refinement on X-ray powder diffraction data [8], the refinement on single-crystal data showed complete ordering of the Ni and Si atoms: three sites are occupied by Ni atoms (16*l*, 16*k*, and 4*d*) and one site by Si atoms (16*l*).

The crystal structure of PrNi$_9$Si$_4$ is a derivative of the cubic NaZn$_{13}$-type. The coordination number of the Pr atoms is 24 and the coordination polyhedron [PrNi$_{16}$Si$_8$] is analogous to the coordination polyhedron of the Na atoms in the NaZn$_{13}$ structure. The coordination number of the Ni1, Ni3, and Si atoms is 13, which is also the case for the Zn atoms in the NaZn$_{13}$ structure. The coordination polyhedron of site Ni3 atom is an icosahedron.

According to [12,13] (which cover data published up to 2000), the structure type NaZn$_{13}$ has three ternary derivatives. The structure of CaCu$_{6.5}$Al$_{6.5}$ [14] is a partly disordered derivative with the same cubic symmetry as the prototype (space group *Fm*-3*c*), whereas the structures of Pr$_{0.693}$Co$_9$Ge$_4$ [15] and CeNi$_{8.5}$Si$_{4.5}$ [5] exhibit tetragonal symmetry (space group *I*4/*mcm*). The arrangement of transition metal and *p*-element atoms is ordered in the former, but partly disordered in the latter.

Table 1 Crystallographic parameters of ternary compounds reported in the Pr–Ni–Si system [2].

Compound	Structure type	Pearson symbol	Space group	*a*, Å	*b*, Å	*c*, Å	Level of structure determination	Method
PrNi$_{7.8}$Si$_{5.2}$	NaZn$_{13}$	*cF*112	*Fm*-3*c*	11.19	–	–	cell	powder
PrNi$_9$Si$_4$	CeNi$_{8.5}$Si$_{4.5}$	*tI*56	*I*4/*mcm*	7.8377	–	11.4861	complete	powder
PrNi$_{8.6}$Si$_{2.4}$	CeNi$_{8.6}$Si$_{2.4}$	*tI*48	*I*4$_1$/*amd*	9.817	–	6.249	cell	powder
Pr$_2$Ni$_{8.5}$Si$_{8.5}$	Th$_2$Ni$_{17}$	*hP*38	*P*6$_3$/*mmc*	8.399	–	8.089	cell	powder
PrNi$_2$Si$_2$	CeAl$_2$Ga$_2$	*tI*10	*I*4/*mmm*	4.047	–	9.621	complete	single-crystal
				4.047	–	9.626	complete	powder
PrNiSi$_2$	CeNiSi$_2$	*oS*16	*Cmcm*	4.1329	16.4453	4.0466	complete	powder
Pr$_3$Ni$_6$Si$_2$	Ce$_3$Ni$_6$Si$_2$	*cI*44	*Im*-3*m*	8.976	–	–	cell	powder
PrNi$_{0.25}$Si$_{1.75}$	α-ThSi$_2$	*tI*12	*I*4$_1$/*amd*	4.187	–	13.846	cell	powder
PrNi$_{0.5-0.75}$×Si$_{1.5-1.25}$	AlB$_2$	*hP*3	*P*6/*mmm*	4.021-4.050	–	4.025-4.181	cell	powder
PrNiSi	LaPtSi	*tI*12	*I*4$_1$*md*	4.109	–	13.970	cell	powder
PrNi$_{1.75}$Si$_{0.25}$	MgZn$_2$	*hP*12	*P*6$_3$/*mmc*	5.227	–	7.709	cell	powder
Pr$_6$Ni$_7$Si$_4$	Pr$_6$Ni$_7$Si$_4$	*oP*68	*Pbcm*	5.888	7.4265	29.558	complete	single-crystal
Pr$_3$NiSi$_3$	Ba$_3$Al$_2$Ge$_2$	*oI*14	*Immm*	4.060	4.277	17.982	complete	powder
Pr$_{14}$Ni$_6$Si$_{11}$	Pr$_{14}$Ni$_6$Si$_{11}$	*mS*124	*C*2/*m*	33.991	4.2328 β = 113.72°	21.330	complete	single-crystal
Pr$_{15}$Ni$_7$Si$_{10}$	Pr$_{15}$Ni$_7$Si$_{10}$	*hP*64	*P*6$_3$/*m*	19.881	–	4.2554	complete	single-crystal
Pr$_7$Ni$_2$Si$_5$	Ce$_7$Ni$_2$Si$_5$	*oP*56	*Pnma*	23.32	4.302	13.84	cell	powder
Pr$_5$Ni$_2$Si$_3$	Ce$_5$Ni$_2$Si$_3$	*hP*40	*P*6$_3$/*m*	15.932	–	4.258	complete	powder
Pr$_5$Ni$_{1.9}$Si$_3$ [a]	La$_5$Ni$_{1.75}$Si$_3$	*hP*44	*P*6$_3$/*m*	15.9268	–	4.2553	complete	single-crystal
Pr$_6$Ni$_2$Si$_3$	Ce$_6$Ni$_2$Si$_3$	*hP*22	*P*6$_3$/*m*	12.005	–	4.273	cell	powder
Pr$_6$Ni$_{1.76}$Si$_3$ [a]	Pr$_6$Ni$_{1.76}$Si$_3$	*hP*24	*P*6$_3$/*m*	12.003	–	4.2939	complete	single-crystal
Pr$_6$Ni$_{1.57}$Si$_3$ [a]	Nd$_6$Ni$_{1.66}$Si$_3$	*hP*26	*P*6$_3$/*m*	12.003	–	4.2939	complete	powder

[a] part of the solid solution of the preceding compound

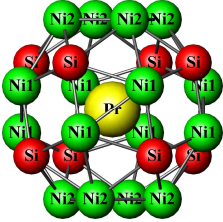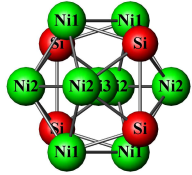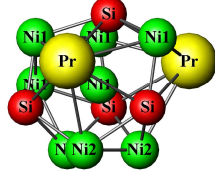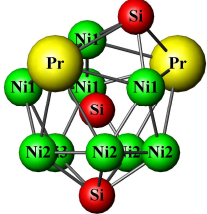**Table 2** Crystal data, data collection and refinement of PrNi₉Si₄.

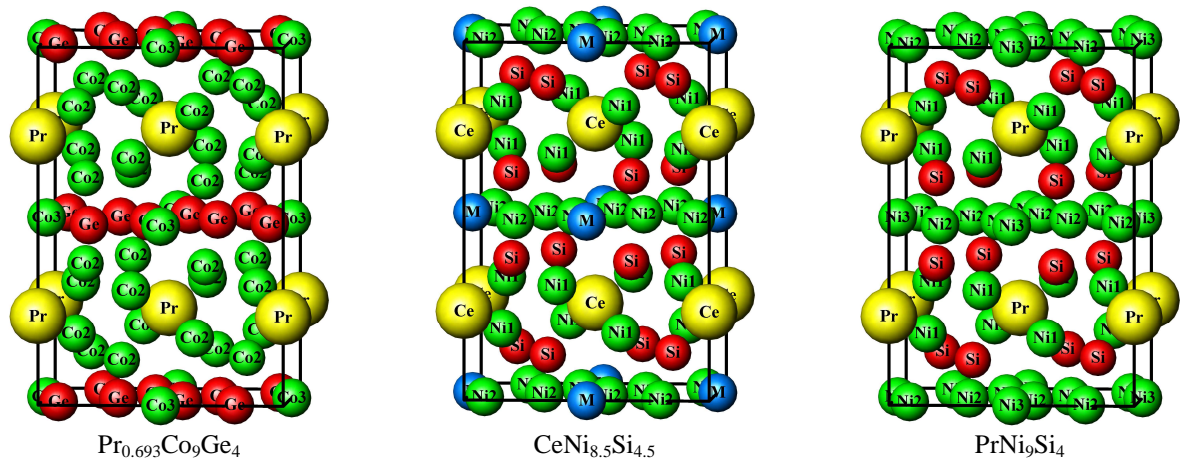|		
Nominal composition of the alloy		$Pr_{7.1}Ni_{60.8}Si_{32.1}$
Refined composition		$PrNi_9Si_4$
Formula weight M_r, g mol^{-1}		781.66
Structure type		$CeNi_{8.5}Si_{4.5}$
Pearson symbol		$tI56$
Space group		$I4/mcm$
Cell parameters:	a, Å	7.8335(11)
	c, Å	11.466(2)
Cell volume V, Å^3		703.6(2)
Formula units per cell Z		8
Density D_X, g cm^{-3}		7.379
Absorption coefficient μ, mm^{-1}		30.853
Temperature, K		295(2)
Crystal shape		needle
Crystal size, mm		0.10×0.035×0.02
Crystal color		metallic gray
Number of reflections:	measured	4421
	independent	264
	with $I > 2\sigma(I)$	209
Reliability factor R_{int}		0.0997
Range of:	h	$-10 \le h \le 10$
	k	$-10 \le k \le 10$
	l	$-14 \le l \le 15$
Refinement on		F^2
Reliability factors:	R (for $I > 2\sigma(I)$)	0.0528 (0.0284)
	wR (for $I > 2\sigma(I)$)	0.0802 (0.0703)
Goodness of fit S		1.106
Number of refined parameters		25
Weighting scheme		$w = 1/[(\sigma F_o)^2 + (0.05P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
Residual electron density:	$\Delta\rho_{max}$, e Å^{-3}	1.383
	$\Delta\rho_{min}$, e Å^{-3}	-1.458

Table 3 Atomic coordinates and displacement parameters for PrNi₉Si₄: structure type CeNi₈.₅Si₄.₅, Pearson symbol *tI*56, space group *I*4/*mcm*, $a = 7.8335(11)$, $c = 11.466(2)$ Å ($a = 7.8377(12)$, $c = 11.4861(17)$ Å, atomic coordinates in italics are from X-ray powder diffraction [8]).

Site	Wyckoff position	x	y	z	$U_{eq.}$, Å^2
Pr	4*a*	0	0	¼	0.0063(4)
Ni1	16*l*	0.63006(13) *0.6302(2)*	0.13006(13) *0.1302(2)*	0.18386(13) *0.18521(17)*	0.0071(4)
Ni2	16*k*	0.06940(19) *0.0691(3)*	0.20269(17) *0.2028(3)*	0	0.0093(4)
Ni3	4*d*	0	½	0	0.0076(6)
Si	16*l*	0.1704(3) *0.1714(4)*	0.6704(3) *0.6714(4)*	0.1195(3) *0.1193(5)*	0.0095(7)

Site	U_{11}, Å^2	U_{22}, Å^2	U_{33}, Å^2	U_{12}, Å^2	U_{13}, Å^2	U_{23}, Å^2
Pr	0.0051(4)	0.0051(4)	0.0087(6)	0	0	0
Ni1	0.0079(6)	0.0079(6)	0.0056(7)	0.0002(5)	-0.0018(4)	0.0018(4)
Ni2	0.0078(8)	0.0090(8)	0.0112(8)	0.0002(6)	0	0
Ni3	0.0070(8)	0.0070(8)	0.0088(13)	0.0031(12)	0	0
Si	0.0097(9)	0.0097(9)	0.0090(16)	0.0021(13)	0.0007(9)	-0.0007(9)

Table 4 Interatomic distances, coordination numbers, and coordination polyhedra for PrNi$_9$Si$_4$.

	Atoms	δ, Å	CN	Polyhedron		Atoms	δ, Å	CN	Polyhedron
Pr	– 8 Ni1	3.1639(9)	24		Ni3	– 4 Si	2.333(3)	12	
	– 8 Si	3.269(3)				– 4 Ni2	2.392(2)		
	– 8 Ni2	3.3217(9)				– 4 Ni1	2.554(1)		
Ni1	– 1 Si	2.298(4)	13		Si	– 1 Ni1	2.298(4)	13	
	– 1 Si	2.330(3)				– 1 Ni1	2.330(3)		
	– 2 Si	2.487(3)				– 1 Ni3	2.333(3)		
	– 2 Ni2	2.527(1)				– 2 Ni2	2.469(3)		
	– 2 Ni1	2.540(1)				– 2 Ni1	2.487(3)		
	– 1 Ni3	2.554(1)				– 2 Ni2	2.529(3)		
	– 1 Ni1	2.883(1)				– 1 Si	2.740(5)		
	– 1 Ni1	3.059(1)				– 2 Pr	3.269(3)		
	– 2 Pr	3.1639(9)				– 1 Si	3.474(5)		
Ni2	– 2 Ni2	2.374(2)	13						
	– 1 Ni3	2.392(2)							
	– 2 Si	2.469(3)							
	– 1 Ni2	2.525(2)							
	– 2 Ni1	2.527(1)							
	– 2 Si	2.529(3)							
	– 2 Pr	3.3217(9)							
	– 1 Ni2	3.357(2)							

Pr$_{0.693}$Co$_9$Ge$_4$ CeNi$_{8.5}$Si$_{4.5}$ PrNi$_9$Si$_4$

Fig. 1 Atom ordering in the structure of PrNi$_9$Si$_4$ compound compared with the models proposed for Pr$_{0.693}$Co$_9$Ge$_4$ and CeNi$_{8.5}$Si$_{4.5}$.

According to [2], less than 20 ternary representatives of the cubic structure type NaZn$_{13}$ have been reported in R–{Fe,Co,Ni}–Si systems (R = La, Ce, Pr, Nd with Fe and Co, R = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy with Ni). In the large majority of the cases only cell parameters have been determined and the parent structure type NaZn$_{13}$ assigned (space group *Fm*-3*c*). The compound LaFe$_{11.5}$Si$_{1.5}$ has,

however, been extensively studied and the structure refined several times. The refinements generally show mixed occupation Fe/Si of the site in Wyckoff position 96*i*, whereas the site in 8*b* is occupied exclusively by Fe atoms. This type of ordering was reported for the first time for CaCu$_{6.5}$Al$_{6.5}$. The situation for the tetragonal derivatives is similar, in the sense that in most cases only cell parameters have

been determined and a reliable classification into different substitution variants cannot be made. Complete structure refinements have been reported for 13 compounds in R–{Fe,Co,Ni}–Si systems [2]. The majority of the compounds have the stoichiometry RT_9Si$_4$ and show the same kind of ordering as found here, with Si occupying one of the sites in Wyckoff position 16l. The ordering model with the same stoichiometry reported for Pr$_{0.693}$Co$_9$Ge$_4$, where Ge occupies the site in Wyckoff position 16k, has not been confirmed and a more recent refinement of the structure of CeCo$_9$Ge$_4$ showed the same type of ordering as observed for the silicides. Differently from the original report on the structure type CeNi$_{8.5}$Si$_{4.5}$, where the excess Si was found in Wyckoff position 4d, more recent refinements on Si-rich compositions in R–{Fe,Co,Ni}–Si systems indicate that the additional Si atoms preferentially substitute on Wyckoff position 16k. It should be noted that a redetermination of the crystal structure of the compound in the Ce–Ni–Si system by Michor *et al.* [16] showed ordered distribution of all the atoms for the composition CeNi$_9$Si$_4$. A narrow homogeneity range CeNi$_{13-x}$Si$_x$ with $x = 4$-4.2 was observed, whereas a wider, off-stoichiometric homogeneity range, $x = 4.2$-5.5, was reported in [17]. The content of the unit cell of the structure of the compound PrNi$_9$Si$_4$ is compared with the ordering models proposed for Pr$_{0.693}$Co$_9$Ge$_4$ and CeNi$_{8.5}$Si$_{4.5}$ in Fig. 1.

The tetragonal structure of PrNi$_9$Si$_4$ can be described as a 3D packing of two types of polyhedron: 24-vertex pseudo Frank-Kasper polyhedra around the rare-earth element atoms in Wyckoff position 4a and icosahedra around the transition metal atoms in Wyckoff position 4d. In the ordered structure of PrNi$_9$Si$_4$ these polyhedra have the compositions [Ni$_{16}$Si$_8$] and [Ni$_8$Si$_4$], respectively.

Conclusions

The crystal structure of the PrNi$_9$Si$_4$ compound was redetermined by X-ray single-crystal diffraction. The structural parameters are in good agreement with those obtained by X-ray powder diffraction. The structure was found to be fully ordered and can be described as a 3D packing of Pr[Ni$_{16}$Si$_8$] pseudo Frank-Kasper polyhedra and Ni[Ni$_8$Si$_4$] icosahedra.

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