Crystal structure and magnetic properties of PrNi$_9$Si$_4$ and NdNi$_9$Si$_4$

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Two rare-earth nickel silicides, PrNi$_9$Si$_4$ and NdNi$_9$Si$_4$, were synthesized. Their crystal structures were refined from X-ray powder diffraction data: structure type CeNi$_{8.5}$Si$_{4.5}$, Pearson symbol $tI56$, space group $I4/mcm$, lattice parameters $a = 7.8377(12)$, $c = 11.4861(17)$ Å for the Pr-containing compound, and $a = 7.836(2)$, $c = 11.457(3)$ Å for the Nd-containing compound. Both structures have a fully ordered distribution of atoms. The two compounds are Curie-Weiss paramagnets due to magnetic moments carried on the rare-earth atoms, with no hint at any magnetic long-range ordering down to 1.72 K.

Introduction

The existence of ternary so-called Ω'-phases, containing 7.1 at.% R with a small homogeneity region near ~30 at.% Si, has been reported in the systems R–Ni–Si (R = La, Ce, Pr, Nd, Sm, Eu) [1]. According to the presented data, the compounds possess a body-centered tetragonal structure ($a = 7.842$, $c = 11.43$ Å for PrNi$_{8.8}$Si$_{4.2}$, and $a = 7.821$, $c = 11.42$ Å for NdNi$_{8.8}$Si$_{4.2}$), derived from the cubic structure type NaZn$_{13}$ (Pearson symbol $cF112$, space group Fm-$3c$ [2]). The same year, the crystal structure of CeNi$_{8.5}$Si$_{4.5}$ was determined (own structure type, Pearson symbol $tI56$, space group $I4/mcm$, partially disordered distribution of Ni and Si atoms) and it was suggested that the Ω'-phases in the other R–Ni–Si systems would be isotypic [3]. During an investigation of the phase equilibria in the Nd–Ni–Si system [4], the Nd-containing phase was assigned the formula NdNi$_{8.5}$Si$_{4.5}$ ($a = 7.821$, $c = 11.16$ Å). According to literature data, in the ternary systems R–Ni–Si (R = Ce, Pr, Nd), the above mentioned ternary phases with tetragonal structure coexist with ternary phases, slightly richer in Si, that adopt the undistorted cubic NaZn$_{13}$ structure type, CeNi$_8$Si$_5$ ($a = 11.15$ Å) [5,6], PrNi$_{7.8}$Si$_{5.2}$ ($a = 11.19$ Å), and NdNi$_{7.8}$Si$_{5.2}$ ($a = 11.16$ Å) [1]. The composition of the cubic Nd-containing compound was reported as NdNi$_{7.6}$Si$_{5.4}$

($a = 11.16$ Å) in [4]. The aim of the present work was to refine the structure of the Ω'-phases existing in the ternary systems {Pr, Nd}–Ni–Si from X-ray powder diffraction, and to study their magnetic behavior. Preliminary results have been reported at two conferences [7,8].

Experimental

Alloys of compositions Pr$_{7.1}$Ni$_{60.8}$Si$_{32.1}$ (PrNi$_{8.5}$Si$_{4.5}$) and Nd$_{7.1}$Ni$_{62.2}$Si$_{30.7}$ (NdNi$_{8.7}$Si$_{4.3}$) were prepared from pieces of the elements of high purity (≥99.8 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To ensure homogeneity, each sample was remelted twice. The composition of the samples was controlled by comparing the mass of the obtained alloys with the total mass of the initial load (~2 g). The mass losses during melting did not exceed 1 %. The alloys were annealed at 600ºC for 2 weeks in evacuated quartz ampoules, and subsequently quenched in cold water.

The quality and the phase purity of the samples were examined on X-ray powder diffraction data collected on a DRON-2.0M diffractometer (Fe $K\alpha$-radiation). The phase analysis indicated single-phase samples containing CeNi$_{8.5}$Si$_{4.5}$-type

compounds. For an accurate refinement of the crystal structures, additional X-ray powder diffraction data were collected at room temperature on an X'pert Pro PANalytical diffractometer with Cu $K\alpha$-radiation. The structures were refined by the Rietveld method (Fig. 1), starting from the coordinates of the prototype CeNi$_{8.5}$Si$_{4.5}$ [3] in space group *I*4/*mcm*, using the FullProf Suite program package [9]. At the first stages of the refinements all of the sites occupied by the smaller atoms in CeNi$_{8.5}$Si$_{4.5}$ were assumed to be occupied by a statistical mixture of Ni and Si. However, the refinements led to complete ordering of the Ni and Si atoms over the four sites (three sites occupied by Ni and one by Si) and the occupancy parameters were fixed in the final cycles of the refinement. Finally, 22 parameters were allowed to vary for each pattern: sample shift, scale factor, two cell parameters, six profile parameters (pseudo-Voigt profile), six positional parameters, five atomic displacement parameters, and one texture parameter. The background was defined by a polynomial function using the Fourier filtering technique. Crystallographic data and details of the data collections and structure refinements for PrNi$_9$Si$_4$ and NdNi$_9$Si$_4$ are listed in Table 1.

Magnetic measurements were carried out in the temperature range 1.72-400 K in magnetic fields up to 5 T, using a commercial SQUID magnetometer.

Results and discussion

The refined atomic coordinates and displacement parameters for the structures of PrNi$_9$Si$_4$ and NdNi$_9$Si$_4$ are listed in Table 2. The structures represent a fully ordered variant of the structure type CeNi$_{8.5}$Si$_{4.5}$ [3]. One site is occupied by the rare-earth atoms (Wyckoff position 4*a*), three sites by Ni atoms (16*l*, 16*k*, and 4*d*) and one site by Si atoms (16*l*). In the structure proposed for the prototype in [3], the site in Wyckoff position 4*d* is occupied by a statistical mixture of Ni and Si atoms in the ratio 1:1. A slightly different
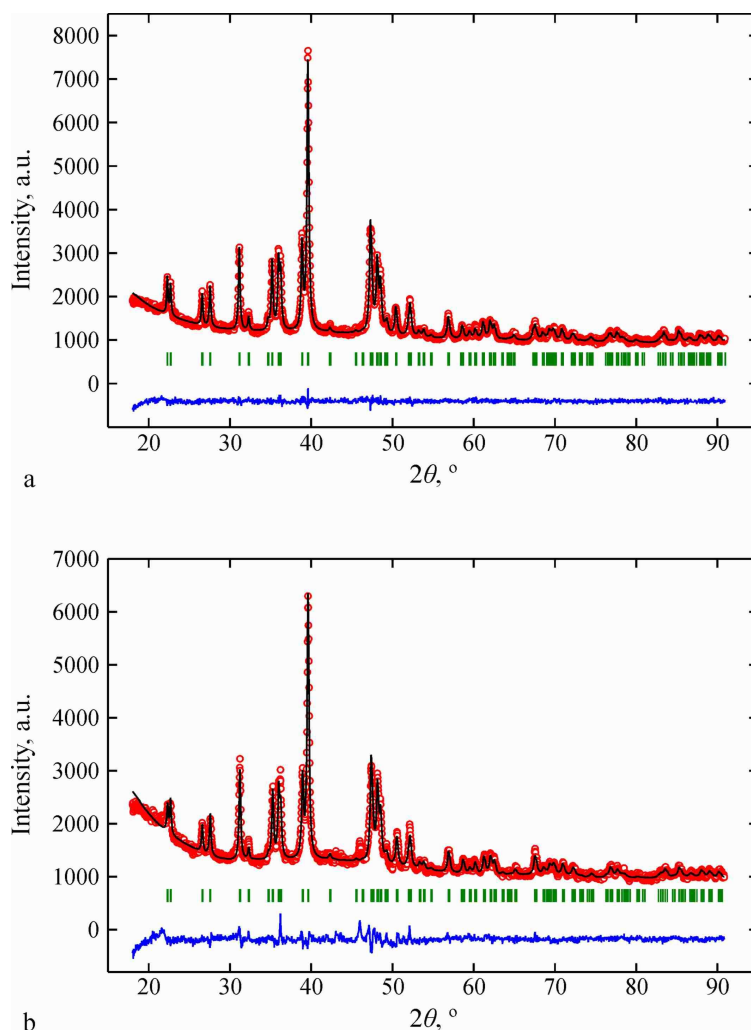
Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the Pr$_{7.1}$Ni$_{60.8}$Si$_{32.1}$ (a) and Nd$_{7.1}$Ni$_{62.2}$Si$_{30.7}$ (b) samples (Cu $K\alpha$-radiation). Vertical bars indicate the positions of reflections for the RNi$_9$Si$_4$ (R = Pr, Nd) compounds.

Table 1 Experimental details and crystallographic data for the compounds $PrNi_9Si_4$ and $NdNi_9Si_4$.

Compound		$PrNi_9Si_4$	$NdNi_9Si_4$
Formula weight M_r		781.49	784.82
Structure type		$CeNi_{8.5}Si_{4.5}$	
Pearson symbol		$tI56$	
Space group		$I4/mcm$	
Unit-cell parameters:	a, Å	7.8377(12)	7.836(2)
	c, Å	11.4861(17)	11.457(3)
Cell volume V, Å³		705.58(18)	703.5(4)
Formula units per cell Z		4	
Density D_X, g cm⁻³		7.3594	7.4126
Preferred orientation: value / [direction]		0.9105(18) / [001]	0.894(3) / [001]
Range 2θ, °		19.00-90.96	
Step size, °		0.026	
Profile parameters	U	-0.02(2)	0.12(5)
	V	0.144(17)	0.03(4)
	W	-0.009(3)	0.020(8)
Shape parameter		1.291(16)	1.19(3)
Asymmetry parameters		0.021(6), 0.0071(14)	0.032(11), 0.011(2)
Number of refined parameters		22	22
Reliability factors:	R_B	0.0288	0.0717
	R_F	0.0239	0.0559
	R_p	0.0211	0.0287
	R_{wp}	0.0264	0.0378
	χ^2	0.929	1.97

Table 2 Atomic coordinates and isotropic displacement parameters for the compounds $PrNi_9Si_4$ and $NdNi_9Si_4$ (structure type $CeNi_{8.5}Si_{4.5}$, Pearson symbol $tI56$, space group $I4/mcm$).

Site	Wyckoff position	x	y	z	B_{iso}, Å²
Pr	4a	0	0	1/4	0.43(5)
Nd					*0.37(9)*
Ni1	16l	0.6302(2)	0.1302(2)	0.18521(17)	0.75(7)
		0.6267(4)	*0.1267(4)*	*0.1866(3)*	*0.90(12)*
Ni2	16k	0.0691(3)	0.2028(3)	0	1.20(8)
		0.0696(5)	*0.2028(5)*		*0.43(12)*
Ni3	4d	0	1/2	0	1.04(12)
					1.1(2)
Si	16l	0.1714(4)	0.6714(4)	0.1193(5)	1.04(13)
		0.1684(8)	*0.6684(8)*	*0.1226(9)*	*2.1(3)*

distribution of Ni and Si atoms was derived from a refinement on neutron diffraction data for a sample of the same composition $CeNi_{8.5}Si_{4.5}$ [10]. The site in $4d$ was found to be occupied exclusively by Ni and the excess Si was localized on the site in $16k$, forming a statistical mixture $Ni_{0.89}Si_{0.11}$ with Ni. A fully ordered atom arrangement was later refined for the composition $CeNi_9Si_4$ [11], but the authors confirm the existence of a small homogeneity range on the Si-rich side and the location of additional Si, when present, in $16k$. As mentioned above, the structure type $CeNi_{9-x}Si_{4+x}$ is a tetragonally distorted derivative of the cubic structure type $NaZn_{13}$ [2]. Another tetragonal derivative of the same structure type was reported for $Pr_{0.7}Co_9Ge_4$ [12]. This structure type has the same space group and atom positions as

$CeNi_{8.5}Si_{4.5}$ ($I4/mcm$), but different distribution of the d- and p-elements: the Ge atoms fully occupy the site in Wyckoff position $16k$ and the Co atoms the remaining sites in $16l$ and $4d$. This structure type must, however, be considered as questionable, since also the refinement of the structure of $CeCo_9Co_4$ on single crystal diffraction data [13] showed full occupancy of the site in $16k$ by Co, whereas the Ge atoms were found to occupy the same $16l$ site as Si in the ordered silicides. As expected, the structures of the compounds $PrNi_9Si_4$ and $NdNi_9Si_4$, determined in this work, exhibit the same kind of ordering of the atoms of the d- and p-elements as observed for $CeNi_9Si_4$ and other silicides and stannides.

The content of the unit cell and the coordination polyhedra in the structure of $NdNi_9Si_4$ are shown in

Fig. 2, and the interatomic distances within the coordination polyhedra are listed in Table 3. The rare-earth atoms center 24-vertex pseudo Frank-Kasper polyhedra [RNi$_{16}$Si$_8$]. The nickel atoms from the site Ni3 (Wyckoff position 4*d*) are surrounded by eight Ni atoms and four Si atoms forming an icosahedron of composition [Ni3Si$_4$Ni$_8$]. The polyhedra of the remaining small atoms (sites Ni1, Ni2, and Si) have 13 vertices ([Ni1Si$_4$Ni$_7$$R_2$], [Ni2Si$_4Ni_7$$R_2$], [SiNi$_9Si_2$$R_2$]) and can be described as distorted icosahedra with one additional atom.

The magnetic properties of PrNi$_9$Si$_4$ and NdNi$_9$Si$_4$ are shown in Fig. 3. Both compounds are strongly temperature dependent paramagnets with no distinct feature in their $\chi(T)$ that might hint at any phase transition at low temperatures (see the upper insets in Fig. 3). In line with the latter conjecture, the isothermal magnetization measured at the terminal temperature of 1.72 K exhibits a behavior characteristic of paramagnets. Above about 50 K, for both compounds, the magnetic susceptibility can be approximated by a modified Curie-Weiss (MCW) law $\chi(T) = \chi_0 + C/(T-\theta)$. The least squares fitting of the MCW formula to the experimental data of PrNi$_9$Si$_4$

yielded the Curie constant $C = 1.475(5)$ (emu K)/mol, the paramagnetic Cure-Weiss temperature $\theta = -3.7(2)$ K, and the temperature independent term $\chi_0 = 8.76(9) \cdot 10^{-4}$ emu/mol. The obtained value of C yields the effective magnetic moment $\mu_{\text{eff}} = 3.43(6)$ μ_B, which is fairly close to the value of 3.58 μ_B expected with the Russell-Saunders (RS) coupling scenario for a free trivalent praseodymium ion. For NdNi$_9$Si$_4$ the derived MCW parameters are: $C = 1.557(6)$ (emu K)/mol, $\theta = -3.2(3)$ K, and $\chi_0 = 7.77(9) \cdot 10^{-4}$ emu/mol. The so-obtained value of $\mu_{\text{eff}} = 3.53(5)$ μ_B is close to the RS prediction of 3.63 μ_B for a Nd^{3+} ion.

The small negative values of θ may signal the presence in the studied materials of some antiferromagnetic correlations, which are, however, apparently too weak to give rise to long-range magnetic ordering above the lowest temperature achievable in the experiments performed here (1.72 K). The χ_0 term is usually considered to be the sum of a diamagnetic contribution due to core-electrons, a paramagnetic contribution due to conduction electrons, and a paramagnetic temperature-independent Van Vleck contribution due to 4*f* states.
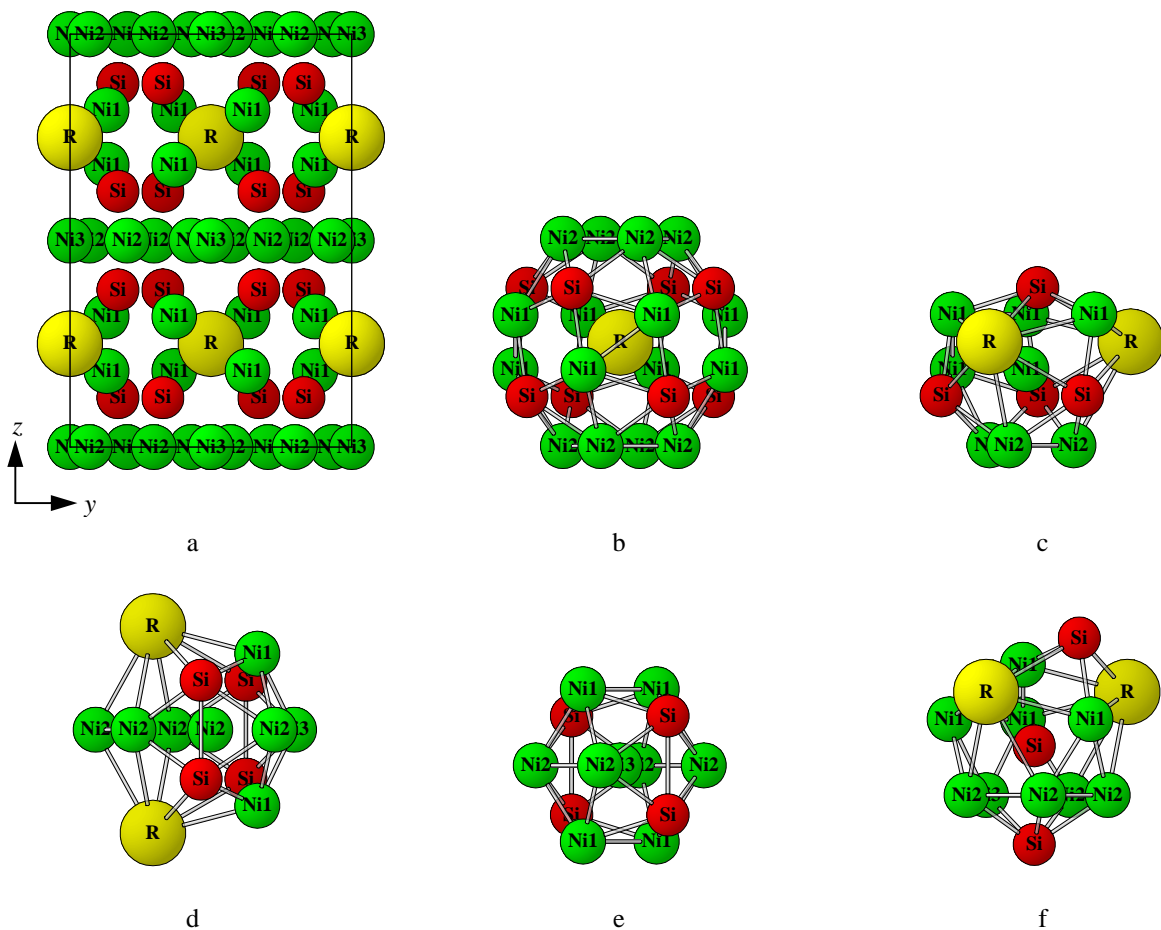

Fig. 2 Unit cell of the RNi$_9$Si$_4$ (R = Pr, Nd) compounds (a) and coordination polyhedra of the atoms: R (b), Ni1 (c), Ni2 (d), Ni3 (e), Si (f).

Table 3 Interatomic distances (δ) and coordination numbers (CN) of atoms for the compounds PrNi$_9$Si$_4$ and NdNi$_9$Si$_4$ (structure type CeNi$_{8.5}$Si$_{4.5}$, Pearson symbol *tI*56, space group *I*4/*mcm*).

Atoms		δ, Å		CN
		R = Pr	R = Nd	
R	− 8 Ni1	3.1616(16)	3.173(3)	
	− 8 Si	3.270(4)	3.260(7)	24
	− 8 Ni2	3.3261(12)	3.321(2)	
Ni1	− 1 Si	2.291(6)	2.234(11)	
	− 1 Si	2.326(4)	2.387(7)	
	− 2 Si	2.503(4)	2.447(7)	
	− 2 Ni1	2.526(2)	2.460(5)	
	− 2 Ni2	2.544(2)	2.560(4)	13
	− 1 Ni3	2.5707(18)	2.558(3)	
	− 1 Ni1	2.886(2)	2.808(4)	
	− 1 Ni1	3.044(2)	3.095(5)	
	− 2 R	3.1616(16)	3.173(3)	
Ni2	− 2 Ni2	2.374(3)	2.376(6)	
	− 1 Ni3	2.392(2)	2.392(4)	
	− 2 Si	2.465(5)	2.503(8)	
	− 1 Ni2	2.529(3)	2.522(6)	
	− 2 Si	2.531(5)	2.544(8)	13
	− 2 Ni1	2.544(2)	2.560(4)	
	− 2 R	3.3261(12)	3.321(2)	
	− 1 Ni2	3.357(3)	3.360(6)	
Ni3	− 4 Si	2.342(4)	2.335(8)	
	− 4 Ni2	2.392(2)	2.392(4)	12
	− 4 Ni1	2.5707(18)	2.558(3)	
Si	− 1 Ni1	2.291(6)	2.234(11)	
	− 1 Ni1	2.326(4)	2.387(7)	
	− 1 Ni3	2.342(4)	2.335(8)	
	− 2 Ni2	2.465(5)	2.503(8)	
	− 2 Ni1	2.503(4)	2.447(7)	
	− 2 Ni2	2.531(5)	2.544(8)	13
	− 1 Si	2.741(8)	2.809(15)	
	− 2 R	3.270(4)	3.260(7)	
	− 1 Si	3.471(7)	3.435(13)	
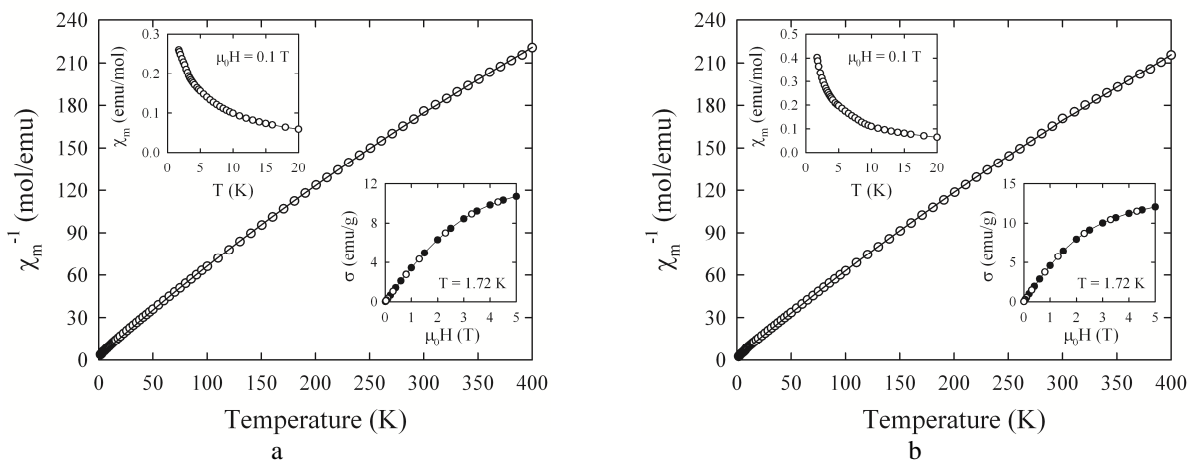
Fig. 3 Temperature dependence of the reciprocal molar magnetic susceptibility of PrNi$_9$Si$_4$ (a) and NdNi$_9$Si$_4$ (b) measured in a field of 0.1 T. The solid lines represent the fits discussed in the text. Upper insets: magnetic susceptibility at low temperatures. Lower insets: field variation of the magnetization measured at 1.72 K with increasing (full circles) and decreasing (open circles) magnetic field strength.

In the present case of $PrNi_9Si_4$ and $NdNi_9Si_4$, the relatively enhanced values of χ_0 likely comprise also a substantial Pauli contribution due to $3d$ states of nickel.

Acknowledgements

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