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Crystal structure of the quaternary phase $Pr(Ni,Al,Ge)_{2-x}$ at the composition $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$

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The crystal structure of $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$ (composition from EDX analysis) has been refined on powder and single-crystal X-ray diffraction data. The solid solution $Pr(Ni,Al,Ge)_{2-x}$, which extends from ternary $Pr(Ni,Ge)_{2-x}$, crystallizes with the hexagonal AlB_2 structure type, Pearson symbol *hP*3, space group *P*6/*mmm*. The refinement on X-ray powder diffraction data led to the composition $PrNi_{0.42}Al_{0.06}Ge_{1.34(2)}$ with 9 % vacancies on the 2-fold site inside the trigonal prisms, a = 4.1622(1), c = 4.2157(2) Å (R_p = 0.0212, R_{wp} = 0.0265, R_B = 0.0742), whereas the composition of the single crystal refined to $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{2.00(1)}$ (a = 4.156(1), c = 4.209(2) Å, R = 0.0275, wR = 0.0516), when the Ni:Al:Ge ratio was fixed to the value found by the EDX analysis.

Praseodymium / Nickel / Alumogermanide / X-ray powder diffraction / X-ray single-crystal diffraction / Crystal structure

Introduction

The isothermal cross-section of the phase diagram of the system Pr–Ni–Al–Ge at approximately 33.3 at.% Pr in the "$PrGe_2$"-rich region at 873 K was investigated in [1]. The formation of solid solutions based on the binary compound $PrGe_{2-x}$ and the ternary compound PrAlGe, both with the tetragonal structure type α-$ThSi_2$, and $Pr(Ni,Ge)_{2-x}$ with hexagonal AlB_2-type structure, was established. The unit-cell parameters and approximate boundaries of the homogeneity range of the AlB_2-type solid solution $Pr(Ni,Ge,Al)_{2-x}$ were determined. It was found that progressive substitution of Ge for Ni or Al "deforms" the trigonal prisms. This can be explained as the result of increasing interaction between *p*-element atoms in the (0 0 1) plane with increasing Ge content. On the contrary, both unit-cell parameters increase monotonically when Ni atoms are replaced by larger Al atoms. A structural investigation of a single crystal of composition $Pr(Ni_{0.2}Al_{0.3}Ge_{0.5})_{1.8}$ showed that the structure was incommensurately modulated in the directions [0 1 0] and [0 0 1] of the parent AlB_2-type structure (a = 4.255(2), c = 4.221(2) Å, $q_1 = 0.169\mathbf{b}^*$, $q_2 = 0.154\mathbf{c}^*$) [2].

Experimental

A sample of nominal composition $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$ was prepared by arc-melting the elements under a purified argon atmosphere. Elements of the following purities were used: Pr 99.9 %, Ni 99.9 %, Al 99.995 %, and Ge 99.999 %. The alloy was annealed at 600°C for 1000 h in an evacuated quartz ampoule, and subsequently quenched in cold water. The mass of the sample was 1 g. The crystal structure was first refined from X-ray powder diffraction data, recorded with a Philips PW1820 diffractometer (Cu $K\alpha$ radiation), using Rietveld refinement routines included in the program package DBWS-9807 [3]. X-ray single crystal diffraction data were then recorded on a STOE Imaging Plate Diffraction System II (Mo $K\alpha$ radiation, graphite monochromator) in the φ-scan mode. An analytical absorption correction was applied, considering the size and the shape of the crystal. The structure was refined by the least-squares method based on $|F^2|$ values, using the SHELXL program [4]. Energy-dispersive X-ray analyses were performed with a Cambridge 438VP microscope coupled to an X-ray detector Noran Pioneer.

Results and discussion

The composition $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$ is at the boundary of the solid solution based on the ternary compound $Pr(Ni,Ge)_{2-x}$ at 33.3 at.% Pr (Fig. 1) [1]. It can be noted that the stoichiometric composition with no vacancies is not known in the ternary system Pr–Ni–Ge, but appears in the quaternary system Pr–Ni–Al–Ge. The result of the microprobe analysis of the investigated sample (Table 1) indicates that the content of Ni and Al is lower, and that of Pr and Ge higher ($Pr_{33.2(2)}Ni_{14.3(3)}Al_{1.5(1)}Ge_{50.0(7)}$), in comparison with the nominal composition of the sample ($Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$). The results of the EDX analysis of selected grains are shown in Table 2, while the EDX spectra and the surface of the sample and are presented in Figs. 2 and 3. It may be noted that the four selected grains, which can be assumed to represent the majority phase, have very similar composition and in all cases contain more than 33.3 at.% Pr. The composition as determined by the energy-dispersive X-ray analysis was obtained by averaging the four compositions: $Pr_{35.1(2)}Ni_{14.8(2)}Al_{1.8(1)}Ge_{48.3(5)}$, and the phase will hereinafter be referred to as $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$.

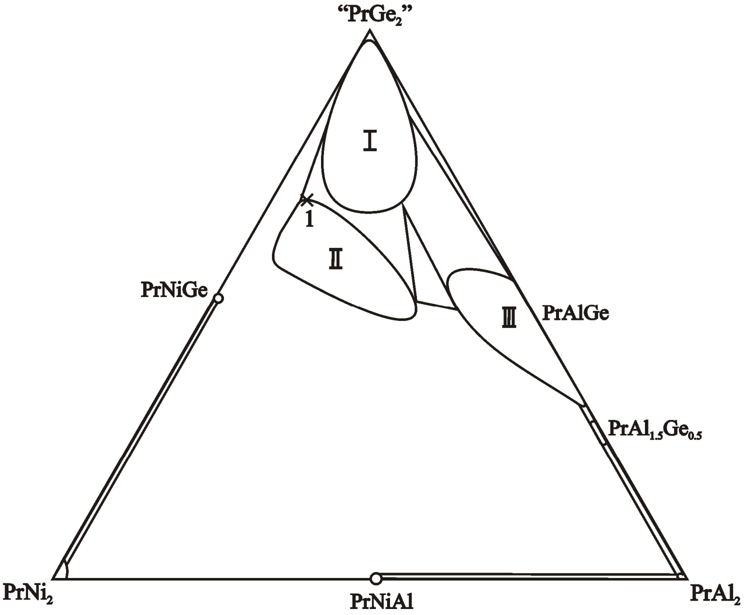

Fig. 1 Isothermal cross-section of the phase diagram of the system Pr–Ni–Al–Ge for 33.3 at.% Pr at 600°C [1] (I – α-$ThSi_2$-type structure, II – AlB_2-type structure, III – α-$ThSi_2$-type structure, 1 – sample of composition $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$), used in the present work.

Table 1 Results of the EDX analysis (global) of the sample $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$.

Element (line)	Intensity	Content [wt.%]	Content [at.%]
Pr (*L*)	176978	51.7(3)	34.2(2)
Ni (*K*)	27450	9.0(2)	14.3(3)
Al (*K*)	1722	0.44(3)	1.5(1)
Ge (*K*)	45335	38.9(5)	50.0(7)

Table 2 Results of the EDX analysis of selected grains of the sample $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$.

Grain	Content [at.%]			
	Pr	Ni	Al	Ge
1	35.6(2)	14.1(2)	1.1(1)	49.3(4)
2	35.0(1)	14.2(2)	1.2(1)	49.6(6)
3	35.2(1)	14.6(2)	1.3(1)	49.5(4)
4	34.7(1)	16.5(2)	3.6(2)	44.9(4)

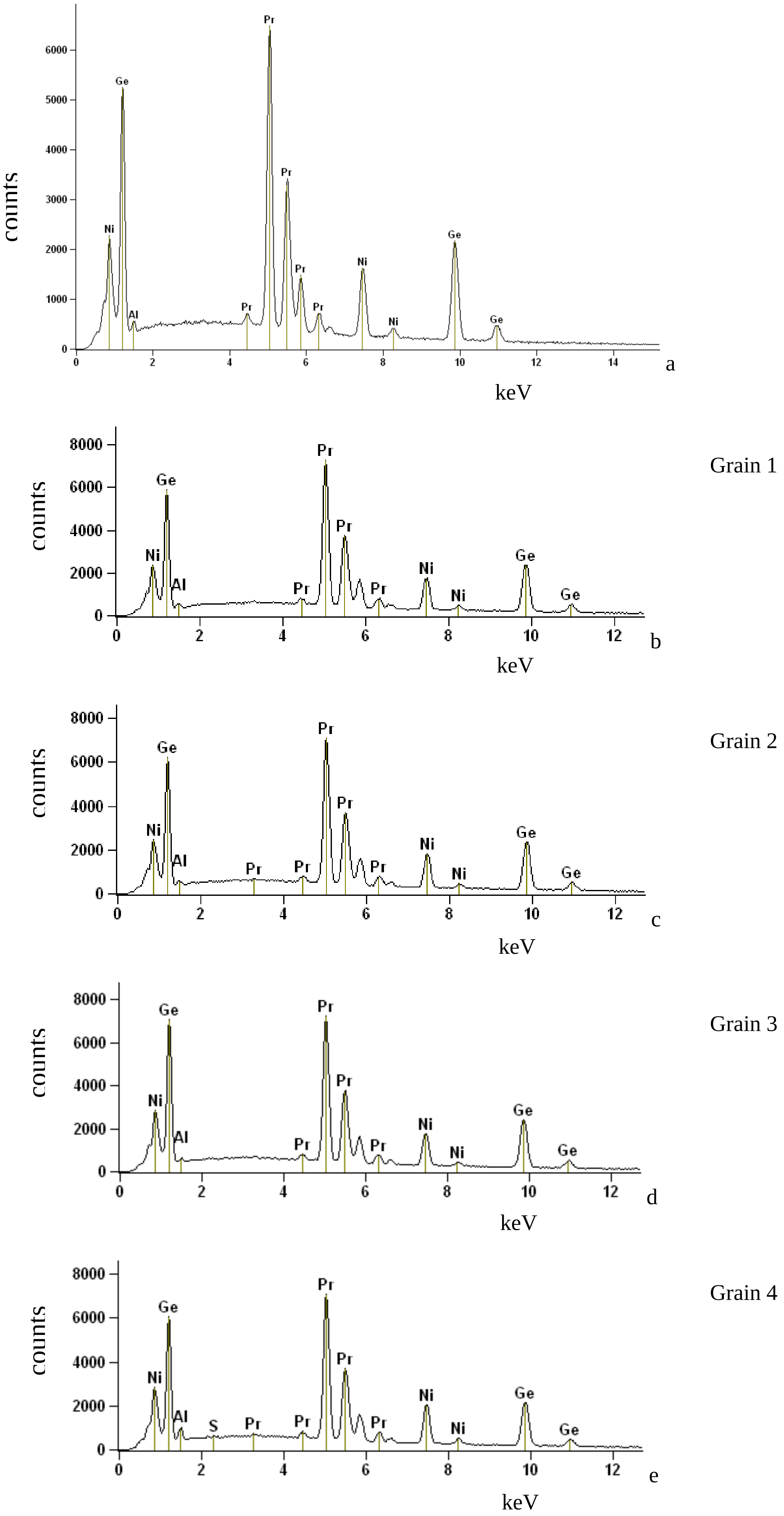

Fig. 2 EDX spectra for the sample $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$ (a) and selected grains of this sample (b-e).

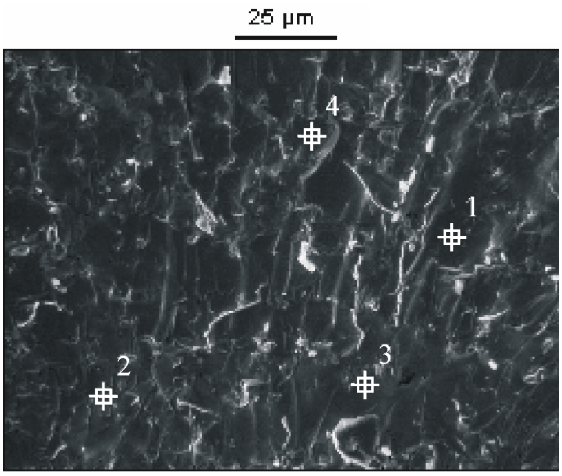

Fig. 3 Surface of the $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$ sample obtained by electron microscopy.

All the strong reflections of the X-ray powder diffraction diagram correspond to a phase with the hexagonal AlB_2 structure type. Additional peaks could be assigned to $PrNi_{0.67}Ge_2$ with the orthorhombic $CeNiSi_2$ structure type. The experimental details of the Rietveld refinement are given in Table 3 and the diffraction diagram is shown in Fig. 4. Fig. 5 shows the content of three unit cells of the structure of $Pr(Ni,Al,Ge)_{2-x}$. For the Pr site (Wyckoff position 1*a*) the occupation was fixed to unity, whereas the Ni:Al ratio of the site in Wyckoff position 2*d* was fixed to the value determined by the EDX analysis. The structural refinement showed that the ratio of Pr with respect to the sum of Ni, Al and Ge differs from the ideal stoichiometry 1:2 and indicates the presence of vacancies on the site occupied by the smaller atoms.

The atomic coordinates and interatomic distances obtained from the refinement on powder diffraction data are presented in Tables 4 and 5. It can be seen that, like the structure of the ternary $Pr(Ni_{0.42-0.28}Ge_{0.58-0.72})_{1.86}$ phase, the structure of $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$ contains a significant amount of vacancies on the site occupied by the smaller atoms. The refined (Ni,Al):Ge ratio was achieved accounting for 9 % vacancies on the 2*d* site. The chemical formula from the refinement can be presented as $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.82}$ (or $Pr_{34.5}Ni_{15.3}Al_{1.7}Ge_{48.5}$, expressed in atomic percent) and is in good agreement with the result of the EDX analysis.

As mentioned above, the sample contained two phases: 89 wt.% $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$ (AlB_2 structure type) and 11 wt.% $PrNi_{0.67}Ge_2$ ($CeNiSi_2$ structure type). The investigation of the phase relations in the quaternary Pr–Ni–Al–Ge system [1] showed that the solid solution based on the $Pr(Ni_{0.42-0.28}Ge_{0.58-0.72})_{1.86}$ phase with AlB_2-type structure (II in Fig. 1) is effectively in equilibrium with the ternary $PrNi_{0.67}Ge_2$ compound with orthorhombic $CeNiSi_2$-type structure. The presence of $PrNi_{0.67}Ge_2$ (27.2 at.% Pr) in a sample of composition $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$ can be understood if the AlB_2-type phase, as indicated by the EDX analysis and the structural refinement, contains more than 33.3 at.% Pr.

The crystal structure of the quaternary AlB_2-type phase was also refined on single-crystal X-ray diffraction data. A single crystal, suitable for the X-ray diffraction investigation, was selected from the same sample of nominal composition $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$. All the reflections of the X-ray single crystal diffraction data could be indexed with a hexagonal cell corresponding to the AlB_2 structure type. Interestingly, the cell parameters of the single crystal (a = 4.156(1), c = 4.209(2) Å) are smaller than those determined by X-ray powder diffraction.

Table 3 Experimental details for the structural refinement on powder diffraction data.

Structure type	AlB_2
Space group	*P*6/*mmm*
a [Å]	4.1622(1)
c [Å]	4.2157(2)
Z	1
Density D_X [g cm^{-3}]	6.940
Preferred orientation parameter [direction]	0.928(5) [100]
Radiation, wavelength [Å]	Cu *K*α, 1.5418
2θ range [°]	10-100.025
Step size [°]	0.025
Profile parameters *U*, *V*, *W*	0.036(2), -0.008(2), 0.0116(4)
Mixing parameter η	0.75(2)
Asymmetry parameter C_M	-0.13(1)
Number of reflections	50
R_B	0.0742
R_p	0.0212
R_{wp}	0.0265
S	1.20
Number of parameters refined	14

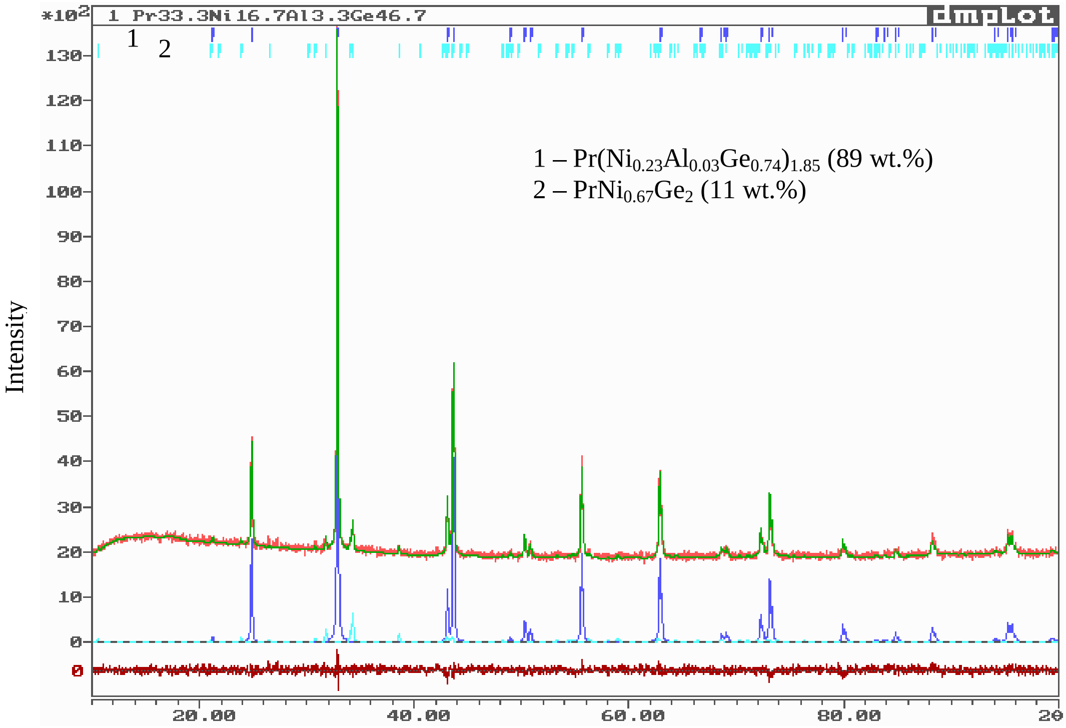

Fig. 4 Observed (dots), calculated (line) and difference (bottom) X-ray diffraction powder patterns for the sample $Pr_{33.3}Ni_{16.7}Al_{3.3}Ge_{46.7}$ annealed at 600°C, Cu $K\alpha$ radiation.

Table 4 Atomic coordinates and isotropic displacement parameters for $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$ (structure type AlB_2, Pearson symbol *hP*3, space group *P*6/*mmm*, a = 4.1622(1), c = 4.2157(2) Å, Z = 1) from the refinement on powder diffraction data.

Atom	Wyckoff position	Atomic coordinates			B_{iso} [Å^2]	Occupancy
		x	*y*	*z*		
Pr	1*a*	0	0	0	0.46(9)	1
Ni	2*d*	⅓	⅔	½	0.9(2)	0.21
Al						0.03
Ge						0.670(9)

Table 5 Interatomic distances in $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$ from the refinement on powder diffraction data.

Atoms		δ [Å]
Pr	–12 *M*	3.196
	–6 Pr	4.162
	–2 Pr	4.216

$M = Ni_{0.21}Al_{0.03}Ge_{0.67}$

Atoms		δ [Å]
M	–3 *M*	2.403
	–6 Pr	3.196

Table 6 Chemical formulas from the refinements on single-crystal diffraction data.

Model	Refined composition
I	$Pr(Ge)_{1.89(2)} \equiv PrGe_{1.89(2)}$
II	$Pr(Al_{0.09(1)}Ge_{0.91(1)})_2 \equiv PrAl_{0.18(2)}Ge_{1.82(2)}$
III	$Pr(Ni)_{0.75(20)}(Ge)_{1.27(15)} \equiv PrNi_{0.75(20)}Ge_{1.27(15)}$
IV	$Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{2.00(3)} \equiv PrNi_{0.46(1)}Al_{0.06(1)}Ge_{1.48(1)}$

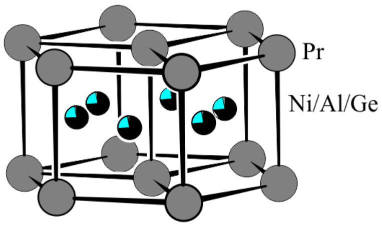

Fig. 5 Crystal structure of Pr(Ni,Al,Ge)$_{2-x}$ (AlB$_2$ structure type).

The refinement of the crystal structure was performed using four different models for the occupation of the site in Wyckoff position 2*d* (Table 6). The first model assumes that Ge atoms alone occupy the position 2*d* (Ge has more electrons than Ni and Al). The second model assumes that position 2*d* is fully occupied by a statistical mixture of Al and Ge atoms (the lightest and the heaviest element), admitting no vacancies. The third model considers a statistical mixture of Ni and Ge atoms, and the total occupancy of site 2*d* is allowed to vary. For the last model the ratio of Ni, Al and Ge atoms was fixed according to the composition of the phase from EDX analysis, and only the total occupancy of the site was refined. The experimental details for the structural refinements are given in Table 7. The atomic coordinates, displacement parameters and interatomic distances are listed in Tables 8 and 9.

Table 7 Experimental details for the structural refinements on single-crystal diffraction data.

Model	I	II	III	IV
Structure type	AlB$_2$			
Space group	*P6/mmm*			
a [Å]	4.156(1)			
c [Å]	4.209(2)			
Z	1			
F(000)	119.5	119.6	121.7	120
D_X [g cm^{-3}]	7.342	7.332	7.370	7.307
μ [mm^{-1}]	41.091	40.313	39.490	39.623
Crystal size [mm]	0.03×0.025×0.006			
Color	gray with metallic luster			
Radiation, wavelength [Å]	Mo *K*α, 0.71073			
θ range [°]	4.84÷34.38			
Range of *h*, *k*, *l*	-3÷6, -6÷6, -5÷6			
Number of measured reflections	626			
Number of independent reflections	75			
Number of reflections with $I > 2\sigma(I)$	72			
R	0.0277	0.0278	0.0273	0.0275
wR	0.0526	0.0527	0.0524	0.0516
S	1.298	1.300	1.290	1.289
Number of reflections used in refinement	75			
Number of parameters refined	7	7	9	7
Weighting scheme	$a = 0.0136$			
$w = 1/[\sigma^2(F_o)^2+(aP)^2+bP]$, $P = [(F_o)^2+2(F_c)^2]/3$	$b = 0.0083$			
$\Delta\rho_{max}$ [e Å^{-3}]	1.688	1.694	1.606	1.650
$\Delta\rho_{min}$ [e Å^{-3}]	-2.523	-2.523	-2.408	-2.461
Extinction parameter	0.14(3)	0.14(3)	0.15(3)	0.14(3)

Table 8 Anisotropic and equivalent isotropic displacement parameters [Å^2] for Pr(Ni,Al,Ge)$_{2-x}$ (structure type AlB$_2$, Pearson symbol *hP*3, space group *P6/mmm*, atoms Pr in 1*a* 0 0 0 and *M* in 2*d* ⅓ ⅔ ½; $U_{22} = U_{11}$, $U_{12} = 1/2U_{11}$, $U_{13} = U_{23} = 0$) from the refinement on single-crystal diffraction data.

Model		I	II	III	IV
M		Ge$_{0.945(10)}$	Al$_{0.09(1)}$Ge$_{0.91(1)}$	Ni$_{0.37(10)}$Ge$_{0.63(8)}$	Ni$_{0.23}$Al$_{0.03}$Ge$_{0.74}$
Pr	$U_{eq.}$	0.0066(4)	0.0066(4)	0.0068(4)	0.0067(4)
	U_{11}	0.0075(4)	0.0075(4)	0.0076(4)	0.0076(4)
	U_{33}	0.0049(5)	0.0049(5)	0.0051(5)	0.0050(5)
M	$U_{eq.}$	0.0128(8)	0.0127(8)	0.0128(8)	0.0127(8)
	U_{11}	0.0131(8)	0.0131(8)	0.0132(8)	0.0131(8)
	U_{33}	0.0120(9)	0.0119(10)	0.0120(10)	0.0119(9)

Table 9 Interatomic distances in $Pr(Ni,Al,Ge)_{2-x}$ from the refinement on single-crystal diffraction data.

Atoms		δ [Å]
Pr	–12 *M*	3.191
	–6 Pr	4.156
	–2 Pr	4.208

Atoms		δ [Å]
M	–3 *M*	2.399
	–6 Pr	3.191

It is not unexpected to see that the four models lead to very similar reliability factors and that the atom/vacancy distribution on site 2*d* has practically no influence on the displacement parameters. However, the refined number of electrons per unit cell (*F*(000), similar for the four models) is larger than for the refinement on powder diffraction data. It may thus be concluded that the single crystal does not have the same composition as the powder. Model IV is probably closest to the real structure, since it contains Ni, Al and Ge in proportions that agree with the chemical analysis. The fact that the refinement on single crystal shows full occupancy of site 2*d* may also explain why no satellites, indicating structural modulations, were observed in the diffraction pattern, since the latter seem to be connected with compositional changes including vacancies.

Conclusions

Satisfactory results cannot be obtained by refining the site occupancies alone when several elements, of which some have similar scattering factors, and possible vacancies are present on the same atom site. The investigation of the crystal structure of the AlB_2-type solid solution extending from $Pr(Ni_{0.42-0.28}Ge_{0.58-0.72})_{2-x}$ into the quaternary Pr–Ni–Al–Ge system was carried out combining X-ray diffraction and EDX analysis. The results concerning the presence of vacancies on the 2-fold site inside the trigonal prisms are not conclusive. 9 % vacancies were found from X-ray powder diffraction data, whereas full occupancy of the same site was found for a single crystal extracted from the same sample. The EDX analysis of selected grains showed an excess of praseodymium, $Pr(Ni_{0.23}Al_{0.03}Ge_{0.74})_{1.85}$, with respect to the nominal composition of the sample (33.3 at.% Pr), which contained 11 wt.% of a secondary phase with less Pr.

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