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Crystal structure of praseodymium germanide $PrGe_{1.91}$

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The structure of the binary germanide $PrGe_{1.910(7)}$ has been determined by single-crystal X-ray diffraction: Pearson symbol *o*S36-12.72, space group *Cmmm*, *a* = 4.2721(6), *b* = 30.673(4), *c* = 4.1433(6) Å, *Z* = 8. The structure is a derivative of the type $TbGe_2$ and related to the types (Sm,Lu)$Ge_{1.85}$ and $DyGe_{1.85}$. These types can be represented as a linear intergrowth of three consecutive AlB_2-type slabs of trigonal prisms and two CaF_2-type slabs.

Germanide / Praseodymium / Single-crystal X-ray diffraction / Crystal structure / Vacancy derivative

1. Introduction

The binary systems *R*–Ge (where *R* is a rare-earth element) have been studied by different groups in order to determine the phase equilibria and the crystal structures of the compounds [1-3]. In all these systems the concentration range 60-66.7 at.% Ge is particularly rich in compounds, which can be expressed by the general formula RGe_{2-x}, where x = 0-0.5. In the structures adopted by the compounds with a high value of x, each Ge atom is surrounded by six larger *R* atoms forming a trigonal prism. "Co-axial" (AlB_2-type [4], all prism axes parallel) and "co-planar" (α-$ThSi_2$-type [5], mutually perpendicular prism axes in consecutive slabs containing prisms with parallel axes) arrangements of fused prisms lead to the formation of 2D- and 3D-networks of Ge-Ge contact distances, respectively, where each Ge atom is surrounded by three other Ge atoms. The deficit of small atoms (Ge) with respect to the parent structure types causes interruptions in the framework, but the basic arrangement of prisms remains and the corresponding character of the Ge-atom substructure is preserved. The structures can be expressed by the general formula $R_{2n+1}X_{3n+2}$, where n = 0 for the parent AlB_2 (space group *P*6/*mmm*) and α-$ThSi_2$ ($I4_1/amd$) types and n > 0 for their vacancy-ordering derivatives [6-11]. Venturini *et al*. distinguished five ordered structures with compositions between $PrGe_{1.56}$ and $PrGe_{1.86}$ within a series of incommensurate derivatives of α-$ThSi_2$ in the Pr–Ge system [9].

Trigonal-prismatic coordination remains for the majority of the Ge atoms in RGe_{2-x} compounds with lower values of x, but a new type of slab appears. In the structures of $TbGe_2$ (space group *Cmmm*) [12], (Sm,Lu)$Ge_{1.85}$ (*Cmcm*) [13], and $DyGe_{1.85}$ ($Cmc2_1$) [14] approximately 3/4 of the Ge atoms are situated inside the trigonal prisms of three consecutive slabs, while the remaining 1/4 of the Ge atoms are placed in two CaF_2-type "semi-octahedral" slabs. The $TbGe_2$ and $DyGe_{1.85}$ structures represent close to ideal variants of Ge atom arrangements in the slabs of trigonal prisms, while the (Sm,Lu)$Ge_{1.85}$ and $PrGe_{1.91}$ structures can be interpreted as vacancy-ordering derivatives.

2. Experimental

The crystal used for the investigation was found in an alloy of nominal composition $Pr_{33.3}Al_5Ge_{61.7}$, prepared from high-purity components (Pr > 99.9, Ge > 99.999, and Al > 99.9989 mass%) by arc melting under protective argon atmosphere with titanium getter; the weight loss was less than 1 mass%. The sample was wrapped in molybdenum foil and annealed in a sealed evacuated silica tube at 1073 K for six weeks, at the end of which it was quenched in cold water. A preliminary phase analysis was carried out on a diffraction pattern recorded with a Debye-Scherrer camera (diameter 53.7 mm) using Cr *K* radiation.

A single crystal with the dimensions 0.02×0.05×0.085 mm was isolated from the annealed alloy. 3124 reflections, indexed on an orthorhombic cell, were collected on an Enraf-Nonius CAD-4 automatic four-circle diffractometer. The crystal structure was solved by direct methods and subsequent least-square refinements were carried out with the SHELX-97 [15] program package. Further details of the data collection and final structure refinement are given in Table 1.

Table 1 Crystal data and details of the data collection and final refinement for $PrGe_{1.91}$.

Composition from refinement		$PrGe_{1.910(7)}$
Molecular mass M_r (g mol^{-1})		279.554
Space group		*Cmmm* (#65)
Cell parameters	*a* (Å)	4.2721(6)
	b (Å)	30.673(4)
	c (Å)	4.1433(6)
Cell volume *V* (Å^3)		542.93(9)
Formula units per unit cell *Z*		8
Density D_x (Mg·m^{-3})		6.840
Radiation, wavelength (Å)		Mo *K*α, 0.71073
Number of reflections for cell parameters		25
Temperature for data collection (K)		293
Crystal size (mm)		0.02×0.05×0.085
Crystal color		gray, metallic
Data collection method		*ω*-2*θ*
Absorption correction		empirical (*ψ*-scans)
Number of measured reflections		3124
Number of independent reflections		504
Refinement on		*F*
Reliability factors	R_F	0.035
	wR	0.050
Number of refined parameters		32

3. Results and discussion

According to the investigation of the Pr–Ge phase diagram by Eremenko *et al.* [16], eight binary compounds form in the system: Pr_3Ge, Pr_5Ge_3, Pr_4Ge_3, Pr_5Ge_4, PrGe, $Pr_{0.9}Ge$, $PrGe_{2-x}$, and $PrGe_2$. A more recent work by Boutarek *et al.* [17], revealed two off-stoichiometric digermanides $PrGe_{2-x}$, which were characterized as two tetragonal α-$ThSi_2$-type phases with different *c*/*a* ratios, called Q_1 and Q_2. Both melt congruently and have significant homogeneity ranges. In a previous work [11] we observed these phases, which were found to exist in the ranges 60-61.8 and 62.7-64.4 at.% Ge, respectively, at 873 K. Fig. 1 shows an extended version of the Pr-Ge phase diagram as determined by Eremenko *et al.* [16], which includes the two nonstoichiometric digermanides $PrGe_{2-x}$ as given in [17], with the homogeneity ranges adjusted to our data [11]. Two of the ordered α-$ThSi_2$ derivatives distinguished by Venturini *et al.* [9] were also identified as identical with Q_1 and Q_2.

Fractional atomic coordinates and displacement parameters for $PrGe_{1.91}$ are presented in Table 2 and Table 3. The positional parameters were standardized with the program STRUCTURE TIDY [18]. The refinement showed no indication for the presence of Al in the structure. The isotropic displacement parameters of sites Ge1 and Ge5 were constrained to be equal.

Table 2 Atom coordinates and site occupancy for $PrGe_{1.91}$

Site	Wyckoff position	*x*	*y*	*z*	Occupancy
Pr1	4*j*	0	0.30943(3)	½	1
Pr2	4*i*	0	0.42367(3)	0	1
Ge1	8*p*	0.1465(17)	0.23939(22)	0	0.218(4)
Ge2	4*k*	0	0	0.0726(9)	½
Ge3	4*j*	0	0.10820(8)	½	1
Ge4	4*i*	0	0.15723(8)	0	1
Ge5	4*i*	0	0.23511(19)	0	0.383(6)
Ge6	4*h*	0.5700(7)	0	½	½

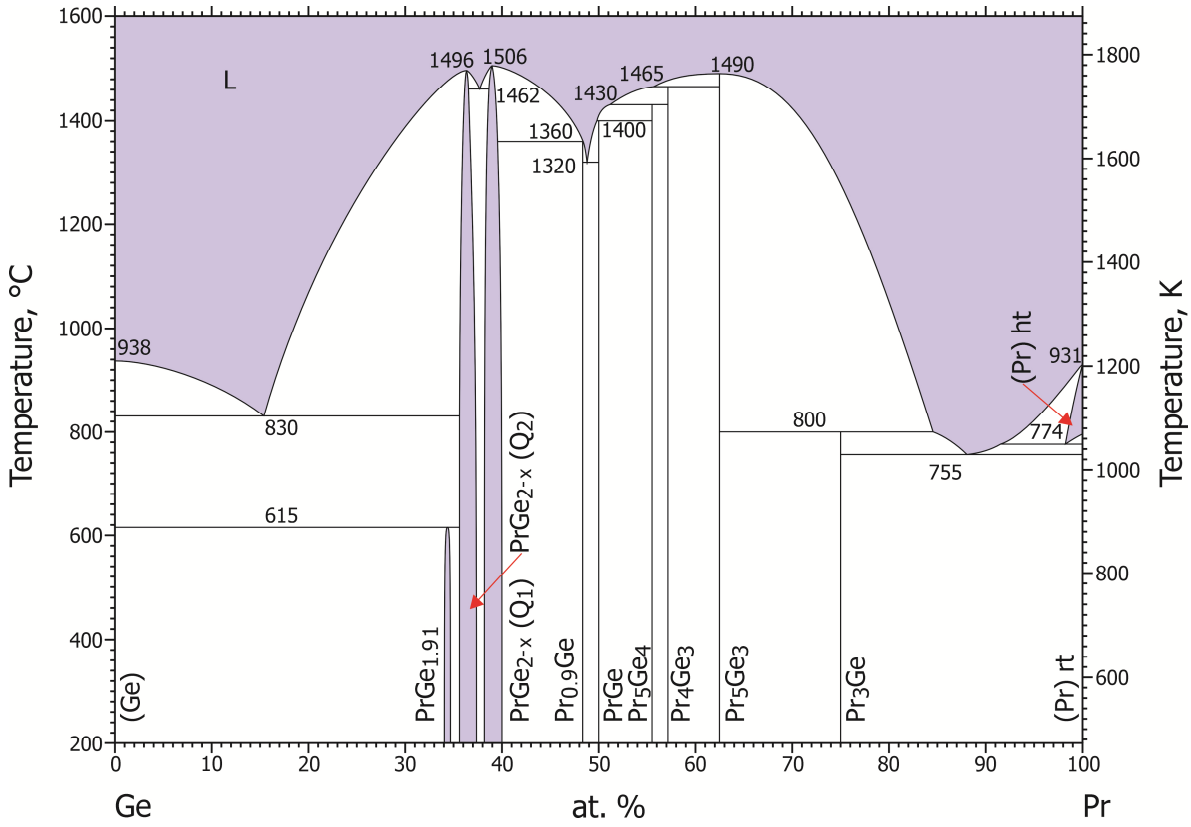

Fig. 1 Pr–Ge phase diagram [16], adjusted with data from [11,17].

Table 3 Equivalent (isotropic) and anisotropic displacement parameters (Å^2) in the structure of $PrGe_{1.91}$.

Atom	B_{eq}/B_{iso}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr1	0.51(2)	0.0074(4)	0.0022(4)	0.0096(4)	0	0	0
Pr2	0.43(2)	0.0073(4)	0.0021(4)	0.0068(4)	0	0	0
Ge1	0.95(7)*						
Ge2	1.17(8)	0.0056(14)	0.0287(21)	0.0103(26)	0	0	0
Ge3	0.89(3)	0.0106(8)	0.0131(9)	0.0101(8)	0	0	0
Ge4	0.91(3)	0.0093(8)	0.0155(10)	0.0097(8)	0	0	0
Ge5	0.95(7)*						
Ge6	0.78(8)	0.0050(25)	0.0151(17)	0.0093(14)	0	0	0

*B_{iso}: $B_{Ge1} = B_{Ge5}$.

Fig. 2 shows a projection of the unit cell of the structure of $PrGe_{1.91}$, along the shortest translation vector, [001].

The interatomic distances within the coordination polyhedra are listed in Table 4. As expected, the structure exhibits several too short distances that, due to the partial occupancies, do not occur in the real structure: between neighboring positions of the split sites Ge2 ($\delta_{Ge2\text{-}Ge2}$ = 0.602(5) Å) and Ge6 ($\delta_{Ge6\text{-}Ge6}$ = 0.598(4) Å), and between Ge5 and Ge1 positions.

The unit-cell parameter ratios of $PrGe_{1.91}$ are similar to those of the types $TbGe_2$, $(Sm,Lu)Ge_{1.85}$, and $DyGe_{1.85}$ (Fig. 3). All these structures contain triple slabs of trigonal prisms, separated by double slabs of "half octahedra". In $TbGe_2$ (Table 5) all the sites inside the trigonal prisms formed by Tb atoms are occupied by Ge atoms with the shortest distances $\delta_{Ge3\text{-}Ge3}$ = 2.107 Å. In $PrGe_{1.91}$, full occupancy of the prismatic sites is observed in the two outer slabs, while the arrangement of Ge atoms in the inner slab is disordered. In total about 2/5 of the trigonal prisms are filled by atoms from the site Ge5, another 2/5 by atoms from the site Ge1, and approximately 1/5 of the prisms are empty.

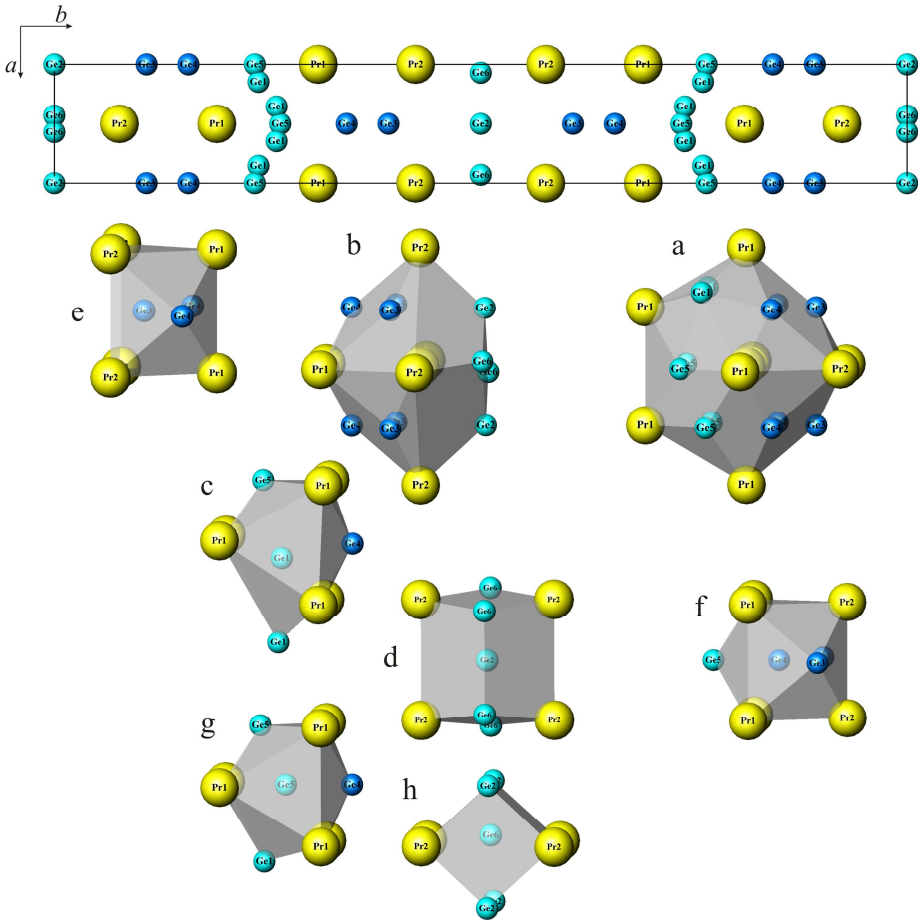

Fig. 2 Projection of the unit cell of the structure of $PrGe_{1.91}$ along [001] and coordination polyhedra: $Pr1Pr_8Ge_{12}$ (a), $Pr2Pr_6Ge_{10}$ (b), $Ge1Pr_6Ge_3$ (c), $Ge2Pr_4Ge_4$ (d), $Ge3Pr_6Ge_2$ (e), $Ge4Pr_6Ge_3$ (f), $Ge5Pr_6Ge_3$ (g), $Ge6Pr_4Ge_4$ (h).

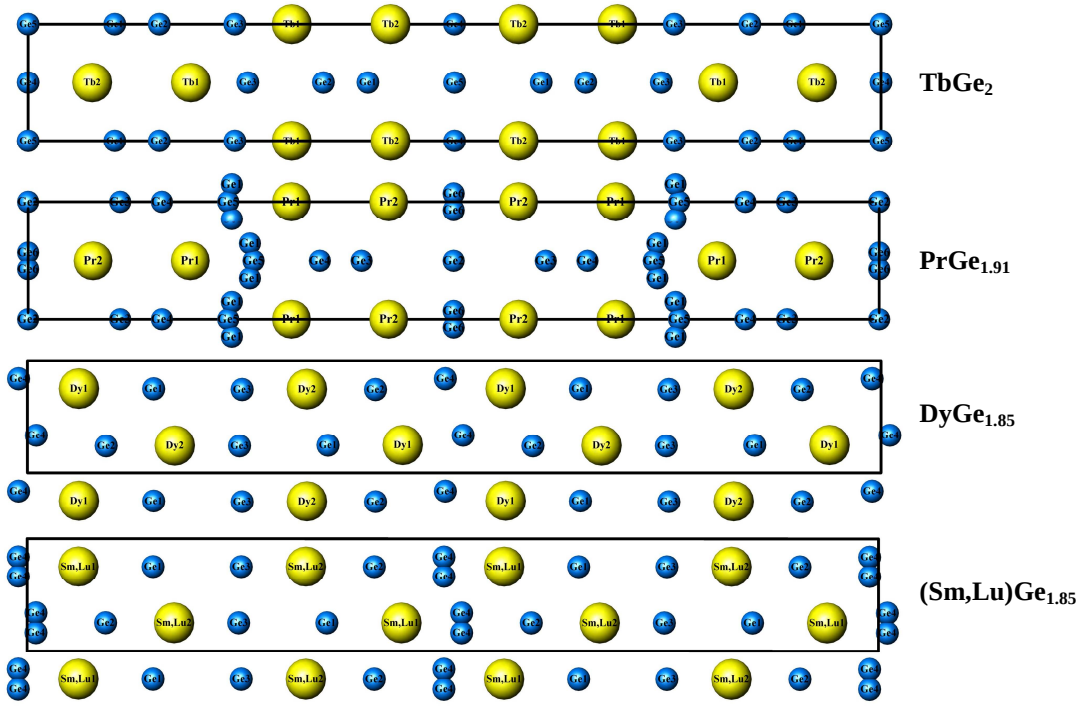

Fig. 3 Projection of the unit cells of $TbGe_2$ and $PrGe_{1.91}$ along [001], and $DyGe_{1.85}$ and $(Sm,Lu)Ge_{1.85}$ along [100].

Table 4 Interatomic distances in the structure of $PrGe_{1.91}$ (split site Ge1 and site Ge5 exclude each other; sites Ge2 and Ge6 are also split).

Atoms		*δ*, Å	Atoms		*δ*, Å
Pr1	- 4 Ge1	2.969(5)	Ge2	- *1 Ge2*	*0.602(5)*
	- 4 Ge1	3.049(5)		- 2 Ge6	2.552(3)
	- 2 Ge5	3.080(4)		- 2 Ge6	3.001(4)
	- 4 Ge4	3.1465(9)		- 2 Ge6	3.011(3)
	- 4 Ge5	3.274(3)		- 4 Pr2	3.1835(8)
	- 2 Ge3	3.309(2)		- 2 Ge6	3.400(3)
	- 4 Ge1	3.763(6)			
	- 2 Pr2	4.0707(12)	Ge3	- 2 Ge4	2.560(2)
	- 2 Pr1	4.1433(6)		- 4 Pr2	3.1321(9)
	- 2 Pr1	4.2255(12)		- 2 Pr1	3.309(2)
	- 2 Pr1	4.2721(6)			
			Ge4	- 1 Ge5	2.389(6)
Pr2	- 4 Ge3	3.1321(9)		- 2 Ge3	2.560(2)
	- 4 Ge6	3.1405(8)		- 2 Ge1	2.597(7)
	- 4 Ge2	3.1835(8)		- 4 Pr1	3.1465(9)
	- 2 Ge4	3.274(2)		- 2 Pr2	3.274(2)
	- 2 Pr1	4.0707(12)			
	- 2 Pr2	4.1433(6)	Ge5	- *2 Ge1*	*0.640(7)*
	- 2 Pr2	4.2721(6)		- *2 Ge1*	*1.701(8)*
				- 2 Ge5	2.323(3)
Ge1	- *1 Ge5*	*0.640(7)*		- 1 Ge4	2.389(6)
	- *1 Ge1*	*1.098(10)*		- 2 Ge1	2.871(7)
	- *1 Ge1*	*1.252(10)*		- 2 Pr1	3.080(4)
	- *1 Ge5*	*1.701(8)*		- 4 Pr1	3.274(3)
	- *2 Ge1*	*2.233(10)*			
	- 1 Ge4	2.597(7)	Ge6	- *1 Ge6*	*0.598(4)*
	- 1 Ge5	2.871(7)		- 2 Ge2	2.552(3)
	- 2 Pr1	2.969(5)		- 2 Ge2	3.001(4)
	- 1 Ge1	3.020(10)		- 2 Ge2	3.011(3)
	- 2 Pr1	3.049(5)		- 4 Pr2	3.1405(8)
	- 2 Pr1	3.763(6)		- 2 Ge2	3.400(3)

Table 5 Relationship between the structures of $TbGe_2$ and $PrGe_{1.91}$ (space group *Cmmm*).

$TbGe_2$ a = 4.113, b = 29.878, c = 4.005 Å					$PrGe_{1.91}$ a = 4.2721, b = 30.673, c = 4.1433 Å					
Site	Wyckoff position and atom coordinates				Site	Wyckoff position and atom coordinates				Occupancy
Tb1	4*j*	0	0.3091	½	Pr1	4*j*	0	0.3094	½	1
Tb2	4*i*	0	0.4249	0	Pr2	4*i*	0	0.4236	0	1
Ge1	4*j*	0	0.1016	½	Ge3	4*j*	0	0.1082	½	1
Ge2	4*i*	0	0.1538	0	Ge4	4*i*	0	0.1573	0	1
Ge3	4*i*	0	0.2424	0	Ge5	4*i*	0	0.2351	0	0.383
					Ge1	8*p*	0.1465	0.2393	0	0.218
Ge4	2*c*	½	0	½	Ge6	4*h*	0.5700	0	½	½
Ge5	2*a*	0	0	0	Ge2	4*k*	0	0	0.0726	½

The average distance between Ge atoms within the central slab is 2.771 Å (Fig. 4), taking into account $\delta_{Ge1\text{-}Ge1}$ = 3.020 Å, which is longer than the usual distances between Ge atoms in germanides (2.4-2.7 Å). Hence, the continuous chain of smaller atoms formed in the structure of $TbGe_2$ (Ge3), appears to be broken into finite four-atom chains in $PrGe_{1.91}$, where two atoms are at the centers of trigonal prisms and two are shifted towards a vacancy. The mean interatomic distance between Ge atoms for such four-member chains, 2.688 Å, is close to the distances between Ge3 and Ge4 atoms in the outer slabs.

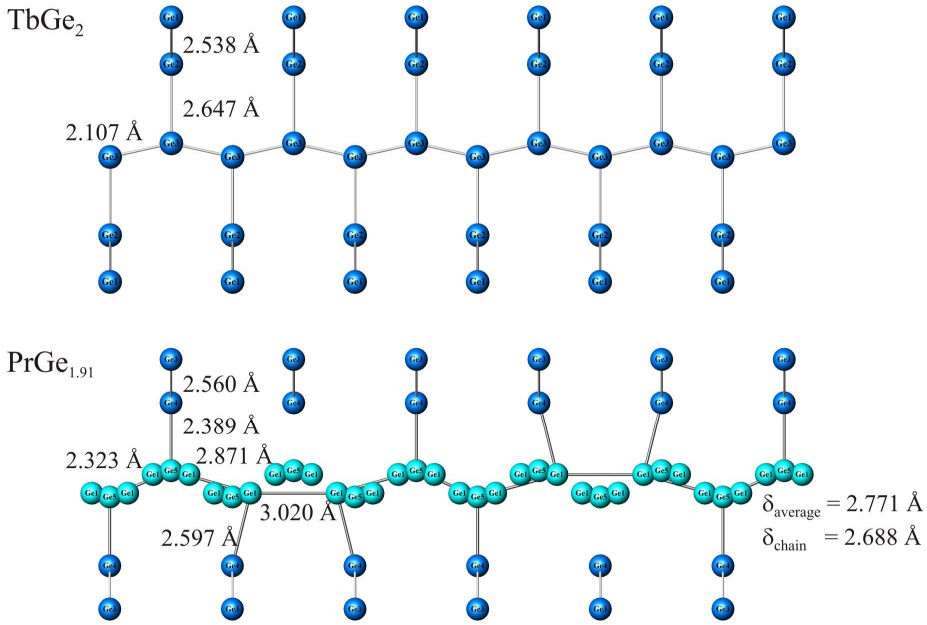

Fig. 4 Ge-atom network in the ordered structure of $TbGe_2$ and part of the corresponding distorted network in $PrGe_{1.91}$ based on realistic distances between partly occupied sites (three consecutive trigonal prism layers are shown in a projection along [001]).

The structure of $(Sm,Lu)Ge_{1.83}$ is an extreme case where Ge-atom chains still exist. 1/3 of the trigonal prisms are empty and only pairs of atoms shifted toward a vacancy remain. Further replacement of small atoms by vacancies leads to the $DyGe_{1.75}$ structure (space group *Cmmm*) [19] with half-occupancy of the Ge sites in the inner trigonal prismatic slab.

The shortest distance between Ge atoms in the CaF_2-type slabs in $TbGe_2$ is 2.871 Å. The unit cell of $PrGe_{1.91}$ is larger and the distance between Wyckoff positions 2*a* and 2*c* has increased to 2.976 Å.

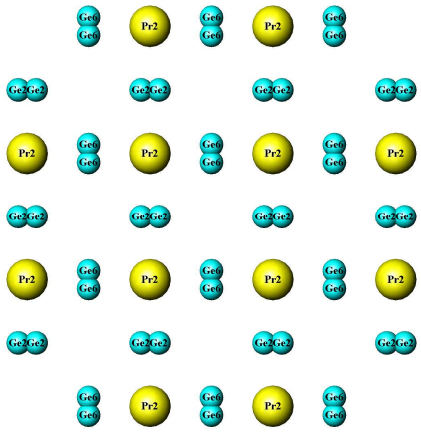

Fig. 5 CaF_2-type slab in the structure of $PrGe_{1.91}$.

In order that Ge-Ge bonds will exist, the Ge atoms are displaced to positions of lower symmetry belonging to half-occupied split sites. The Ge atoms form distorted squares in the plane perpendicular to the crystallographic direction [010] (Fig. 5) with Ge-Ge distances of 2.552 Å.

Conclusions

The structure of the binary germanide $PrGe_{1.91}$ has been determined by single-crystal X-ray diffraction. It is a partly disordered derivative of the $TbGe_2$ type and can be represented as a linear intergrowth of three AlB_2-type slabs of trigonal prisms stacked as in α-$ThSi_2$ (mutually perpendicular prism axes in neighboring slabs) and two CaF_2-type slabs. Both structure types are closely related to the structures of $(Sm,Lu)Ge_{1.85}$ and $DyGe_{1.85}$ with similar cell parameters. The latter are built from the same type of slab, however the axes of the trigonal prisms in neighboring AlB_2-type slabs are all parallel, as in AlB_2 itself.

Vacancies in the Ge substructure and the consecutive deformations favor bonding between Ge atoms and lead to the formation of finite chains and squares in the structure of $PrGe_{1.91}$.

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