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Structure refinements of the compounds Pr_5Si_3 and Zr_3Si_2

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The structures of the compounds Pr_5Si_3 and Zr_3Si_2 were refined on X-ray single-crystal diffraction data. Pr_5Si_3 crystallizes with the tetragonal structure type Cr_5B_3: space group *I*4/*mcm*, Pearson symbol *tI*32, $a = 0.7820(1)$, $c = 1.3812(3)$ nm, $Z = 4$, $R1 = 0.035$, $wR2 = 0.080$ for 287 unique reflections, 16 refined parameters. Zr_3Si_2 crystallizes with the tetragonal structure type U_3Si_2: Pearson symbol *tP*10, space group *P*4/*mbm*, $a = 0.7087(1)$, $c = 0.37060(7)$ nm, $Z = 2$, $R1 = 0.022$, $wR2 = 0.042$ for 114 unique reflections, 12 refined parameters.

Praseodymium / Zirconium / Silicide / Arc-melting / High-frequency furnace / Crystal structure / X-ray diffraction

Introduction

Interest in zirconium silicides is mainly based on their potential applications, for example as neutron reflectors. According to an investigation of Zr_3Si_2 for nuclear applications [1], this compound fulfills the requirements for gas fast reactors, for which good thermal conductivity is particularly needed. Silicides of rare-earth metals are interesting due to their magnetic properties [2,3]; they may find application in microelectronic devices, integrated circuits and as materials for magnetic refrigeration.

The binary Pr–Si [4] and Zr–Si [5,6] systems have been studied and the phase diagrams constructed in the whole concentration range. Seven binary compounds have been reported in the Pr–Si system [7,8]: Pr_5Si_3 (the room-temperature modification belongs to the structure type Cr_5B_3), Pr_3Si_2 (U_3Si_2), Pr_5Si_4 (Zr_5Si_4), PrSi (FeB), $Pr_2Si_{2.72}$ (V_2B_3), $PrSi_{1.63}$ (α-$GdSi_2$), and $PrSi_{2-1.70}$ (α-$ThSi_2$). Seven binary compounds exist in the Zr–Si system [7,8]: Zr_3Si (structure type Ti_3P), Zr_2Si ($CuAl_2$), Zr_5Si_3 (Mn_5Si_3), Zr_3Si_2 (U_3Si_2), Zr_5Si_4 (the room-temperature modification with own structure type), ZrSi (the high-temperature modification belongs to the structure type TlI (CrB), the room-temperature modification belongs to the structure type FeB), and $ZrSi_2$ (own structure type). Selected crystallographic data for the binary compounds in the Pr–Si and Zr–Si systems are listed in Table 1.

In [16] the structure of the binary compound Zr_3Si_2 was studied on powder diffraction data and the unit-cell parameters were refined (Table 2). The unit-cell parameters of the Pr_5Si_3 compound have several times been refined on polycrystalline samples [3,13,20-27]. In [2] the crystal structure was determined on single crystals grown by the floating zone technique with optical heating. In the present work the crystal structures of both Pr_5Si_3 and Zr_3Si_2 were determined from X-ray single-crystal diffraction data.

Experimental

During an investigation of the ternary system Pr–Zr–Si, a sample of nominal composition $Pr_{40}Zr_{20}Si_{40}$ was prepared by arc-melting the elements under a purified argon atmosphere. The mass of the sample was 1 g. Elements of the following purities were used: Pr 99.85 %, Zr 99.9 %, and Si 99.999 %. The single crystal of the Pr_5Si_3 compound was selected from the as-cast alloy, whereas the single crystal of the Zr_3Si_2 compound was obtained after heating and slow cooling of the sample in an evacuated Ta-container in a high-frequency furnace. X-ray single-crystal diffraction data were recorded at room temperature on a STOE Imaging Plate Diffraction System II (Mo *K*α radiation, plane graphite monochromator) in the φ-scan mode. An analytical absorption correction was applied considering the size and the shape of the crystals. The starting atomic

Table 1 Cell parameters of the binary compounds in the Pr–Si and Zr–Si systems.

Compound	Structure type	Pearson symbol	Space group	Cell parameters (nm)			Literature
				a	*b*	*c*	
α-Pr_5Si_3	Cr_5B_3	*tI*32	*I*4/*mcm*	0.78172	–	1.3816	[2]
Pr_3Si_2	U_3Si_2	*tP*10	*P*4/*mbm*	0.775	–	0.438	[9]
Pr_5Si_4	Zr_5Si_4	*tP*36	$P4_12_12$	0.79092	–	1.49437	[10]
PrSi	FeB	*oP*8	*Pnma*	0.824	0.3941	0.592	[11]
$Pr_2Si_{2.72}$	V_2B_3	*oS*20	*Cmcm*	0.43834	2.47200	0.39326	[12]
$PrSi_{1.63}$	α-$GdSi_2$	*oI*12	*Imma*	0.4162	0.4103	1.3827	[13]
$PrSi_{2-1.70}$	α-$ThSi_2$	*tI*12	$I4_1/amd$	0.4201-0.4163	–	1.3744-1.3754	[13]
Zr_3Si	Ti_3P	*tP*32	$P4_2/n$	1.101	–	0.545	[14]
Zr_2Si	$CuAl_2$	*tI*12	*I*4/*mcm*	0.6581	–	0.5372	[15]
Zr_5Si_3	Mn_5Si_3	*hP*16	$P6_3/mcm$	0.7886	–	0.5558	[15]
Zr_3Si_2	U_3Si_2	*tP*10	*P*4/*mbm*	0.7082	–	0.3714	[16]
α-Zr_5Si_4	Zr_5Si_4	*tP*36	$P4_12_12$	0.71225	–	1.3000	[17]
β-ZrSi	TlI	*oS*8	*Cmcm*	0.3762	0.9912	0.3754	[16]
α-ZrSi	FeB	*oP*8	*Pnma*	0.6995	0.3786	0.5296	[18]
$ZrSi_2$	$ZrSi_2$	*oS*12	*Cmcm*	0.372	1.476	0.367	[19]

Table 2 Cell parameters reported for Pr_5Si_3 and Zr_3Si_2 in the literature.

Compound	Cell parameters (nm)		V (nm^3)	Literature
	a	*c*		
Pr_5Si_3	0.793	1.397	0.87850	[20]
	0.7812	1.375	0.83913	[21]
	0.781	1.374	0.83809	[22]
	0.7814	1.374	0.83895	[23]
	0.7812	1.3772	0.84047	[24]
	0.7871	1.3863	0.85885	[25]
	0.78192	1.3791	0.84318	[26]
	0.78172 [a]	1.3816 [a]	0.84428 [a]	[2]
	0.78089	1.37510	0.83852	[3]
	0.7827	1.379	0.84480	[13]
	0.7814	1.3754	0.83980	[27]
Zr_3Si_2	0.7082	0.3714	0.18627	[16]

[a] single-crystal data

parameters were deduced by direct methods with the SHELXS-97 program [28]. The thermal motion of the atoms was described by anisotropic displacement parameters for all of the sites. Experimental details for the structure refinements with the SHELXL-97 program [28] (full-matrix least-squares refinement based on $|F^2|$ values) are given in Table 3.

Since the single crystals were selected from a ternary alloy, we checked the solubility of the third component in the compounds Pr_5Si_3 and Zr_3Si_2. No statistical mixture was found on any atom site in the structures and the structure refinements confirmed that each site is occupied by one single type of atom.

Results and discussion

Pr_5Si_3 crystallizes with the tetragonal structure type Cr_5B_3: Pearson symbol *tI*32, space group *I*4/*mcm*, $a = 0.7820(1)$, $c = 1.3812(3)$ nm, $Z = 4$, $R1 = 0.035$, $wR2 = 0.080$ for 287 reflections with $I > 2\sigma(I)$, 16 refined parameters. Zr_3Si_2 crystallizes with the tetragonal structure type U_3Si_2: Pearson symbol *tP*10, space group *P*4/*mbm*, $a = 0.7087(1)$, $c = 0.37060(7)$ nm, $Z = 2$, $R1 = 0.022$, $wR2 = 0.042$ for 114 reflections with $I > 2\sigma(I)$, 12 refined parameters. The results obtained here are in good agreement with previous studies. The contents of the unit cells of the structures of Pr_5Si_3 and Zr_3Si_2 and the coordination polyhedra of the atoms are shown in Figs. 1 and 2. The atomic coordinates, displacement parameters and interatomic distances are listed in Tables 4-6. Both structure types belong to the category of structures with trigonal-prismatic coordination of the smaller atoms according to the classification by P.I. Kripyakevich [29].

The tetragonal structure type Cr_5B_3 is characterized by the stacking of fragments of the U_3Si_2 and $CuAl_2$ types along the four-fold axis.

Table 3 Experimental details for the structure refinements of Pr_5Si_4 and Zr_3Si_2.

Chemical formula	Pr_5Si_3	Zr_3Si_2
Structure type	Cr_5B_3	U_3Si_2
Pearson symbol	*tI*32	*tP*10
Space group	*I*4/*mcm*	*P*4/*mbm*
Molar mass	788.82	329.84
a (nm)	0.7820(1)	0.7087(1)
c (nm)	1.3812(3)	0.37060(7)
V (nm^3)	0.8446(2)	0.18614(5)
Z	4	2
F(000)	1348	296
D_x ($g\ cm^{-3}$)	6.203	5.885
μ (mm^{-1})	28.62	8.63
Radiation, wavelength (nm)	Mo *K*α, 0.071073	
θ range (°)	3.0-29.2	4.1-29.2
Range of *h*, *k*, *l*	-7-7, 0-10, 0-18	-6-6, 0-9, 0-5
Number of measured reflections	561	268
Number of independent reflections	332	159
Number of reflections with $I > 2\sigma(I)$	287	114
*R*1, *wR*2 for $I \geq 2\sigma(I)$	0.035, 0.080	0.022, 0.042
*R*1, *wR*2 for all data	0.044, 0.083	0.050, 0.046
Goodness of fit *S*	1.16	0.77
Number of reflections used in the refinement	332	159
Number of refined parameters	16	12
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	2.27, -4.18	1.05, -1.04
Extinction parameter	0.0017(2)	0.0093(17)

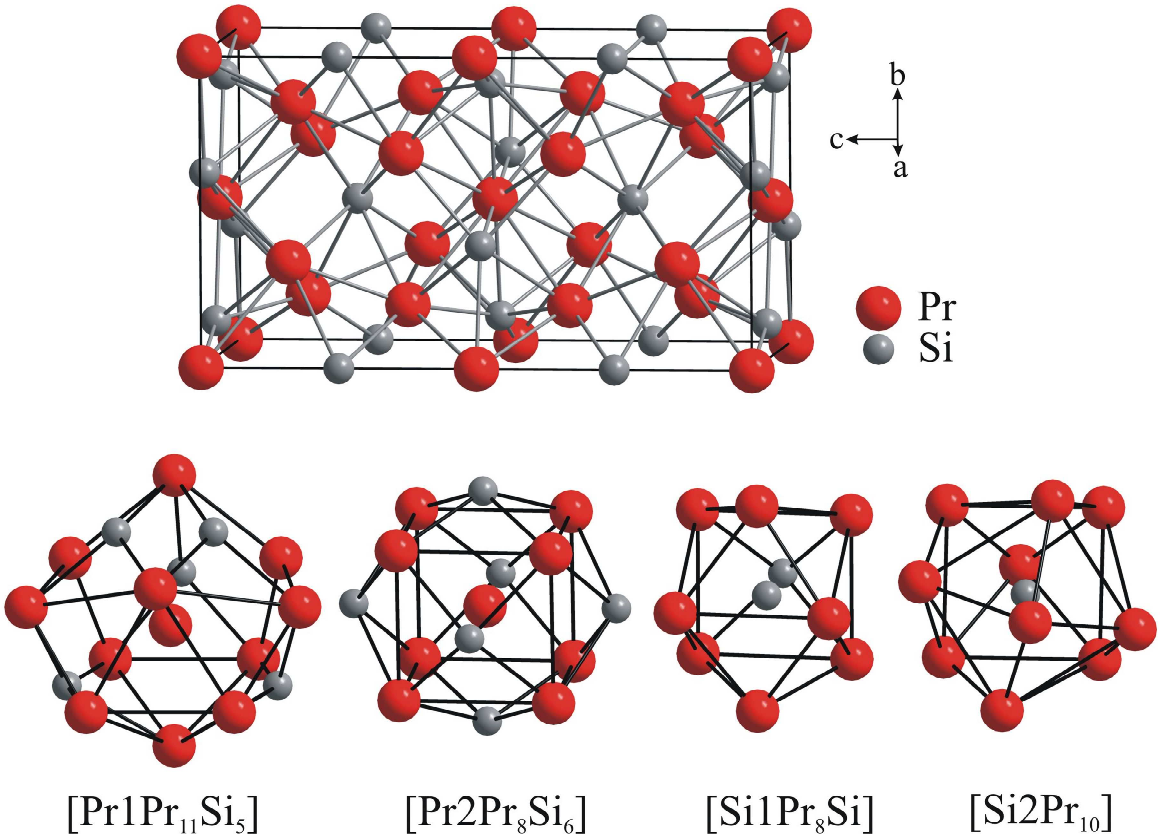

Fig. 1 Unit-cell content of the structure of Pr_5Si_3 and coordination polyhedra of the atoms.

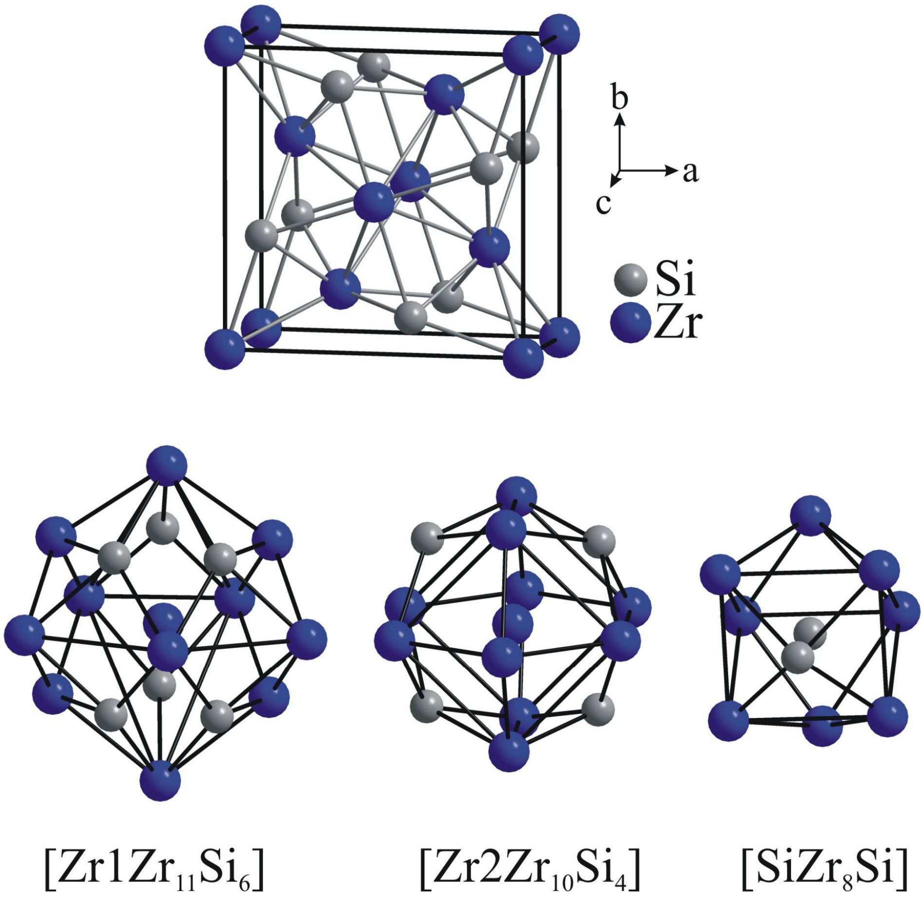

Fig. 2 Unit-cell content of the structure of Zr_3Si_2 and coordination polyhedra of the atoms.

Table 4 Atomic coordinates and isotropic displacement parameters for Pr_5Si_3 (Pearson symbol *tI*32, structure type Cr_5B_3, space group *I*4/*mcm*, $a = 0.7820(1)$, $c = 1.3812(3)$ nm, $Z = 4$) and Zr_3Si_2 (Pearson symbol *tP*10, structure type U_3Si_2, space group *P*4/*mbm*, $a = 0.7087(1)$, $c = 0.37060(7)$ nm, $Z = 2$).

Compound	Site	Wyckoff position	*x*	*y*	*z*	U_{eq} (Å^2)
Pr_5Si_3	Pr1	16*l*	0.17562(5)	0.67562(5)	0.14703(4)	0.0113(3)
	Pr2	4*c*	0	0	0	0.0241(4)
	Si1	8*h*	0.6154(4)	0.1154(4)	0	0.0103(8)
	Si2	4*a*	0	0	¼	0.012(1)
Zr_3Si_2	Zr1	4*h*	0.1739(1)	0.6739(1)	½	0.0041(4)
	Zr2	2*a*	0	0	0	0.0038(3)
	Si	4*g*	0.6229(3)	0.1229(3)	0	0.0036(6)

Table 5 Anisotropic displacement parameters (Å^2) for Pr_5Si_3 and Zr_3Si_2.

Compound	Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr_5Si_3	Pr1	0.0114(3)	0.0114(3)	0.0109(4)	0.0005(2)	-0.0005(2)	-0.0005(2)
	Pr2	0.0093(4)	0.0093(4)	0.054(1)	0	0	0
	Si1	0.009(1)	0.009(1)	0.013(2)	0.001(1)	0	0
	Si2	0.010(2)	0.010(2)	0.014(3)	0	0	0
Zr_3Si_2	Zr1	0.0039(4)	0.0039(4)	0.0034(6)	0.0001(4)	0	0
	Zr2	0.0033(5)	0.0033(5)	0.0058(9)	0	0	0
	Si	0.0038(9)	0.0038(9)	0.0033(2)	-0.0002(9)	0	0

Table 6 Interatomic distances for Pr_5Si_3 and Zr_3Si_2.

Atoms		δ (nm)
Pr1	-1 Si1	0.3077(3)
	-2 Si1	0.3086(2)
	-2 Si2	0.32161(5)
	-1 Pr1	0.3286(1)
	-2 Pr2	0.35277(5)
	-1 Pr1	0.3884(1)
	-2 Pr1	0.3954(1)
	-1 Pr1	0.4062(1)
	-4 Pr1	0.4079(1)
Zr1	-2 Si	0.2754(3)
	-4 Si	0.2826(2)
	-4 Zr2	0.32085(5)
	-1 Zr1	0.3485(2)
	-4 Zr1	0.3704(1)
	-2 Zr1	0.3706(1)
Zr2	-4 Si	0.2811(2)
	-8 Zr1	0.32085(5)
	-2 Zr2	0.3706(1)
Pr2	-4 Si1	0.3140(2)
	-2 Si2	0.34530(7)
	-8 Pr1	0.35277(5)
Si1	-1 Si1	0.2552(9)
	-2 Pr1	0.3077(3)
	-4 Pr1	0.3086(2)
	-2 Pr2	0.3140(2)
Si2	-8 Pr1	0.32161(5)
	-2 Pr2	0.34530(7)
Si	-1 Si	0.2464(6)
	-2 Zr1	0.2754(3)
	-2 Zr2	0.2811(2)
	-4 Zr1	0.2826(2)

The structure of the Pr_5Si_3 compound belongs to the Cr_5B_3 type with Pr atoms in the Cr sites and Si atoms in the B sites. The Si1 atoms (at the canters of trigonal prisms) are bonded in pairs ($\delta_{Si1\text{-}Si1}$ = 0.2552(9) nm), whereas the Si2 atoms (at the canters of square antiprisms) are isolated from each other and form straight chains with Pr2 atoms ($\delta_{Si2\text{-}Pr2}$ = 0.34530(7) nm) along the crystallographic direction [001]. The coordination numbers of the sites Pr1, Pr2, Si1, and Si2 in the structure of Pr_5Si_3 are 16, 14, 9, and 10, respectively. The Pr2 atoms are located inside cubes formed by eight Pr1 atoms ($\delta_{Pr2\text{-}Pr1}$ = 0.35277(5) nm), the faces of which are capped by six Si atoms forming an octahedron. The octahedron is elongated along the [001] direction, and the distances between Pr2 and the equatorial Si1 atoms are 0.3140(2) nm, whereas those between Pr2 and the axial Si2 atoms are 0.34530(7) nm (Fig. 3). This explains the relatively large value observed for the anisotropic displacement parameter U_{33}. The Si1 atoms are located inside trigonal prisms formed by Pr atoms, the rectangular faces of which are capped by one Si and two Pr atoms.

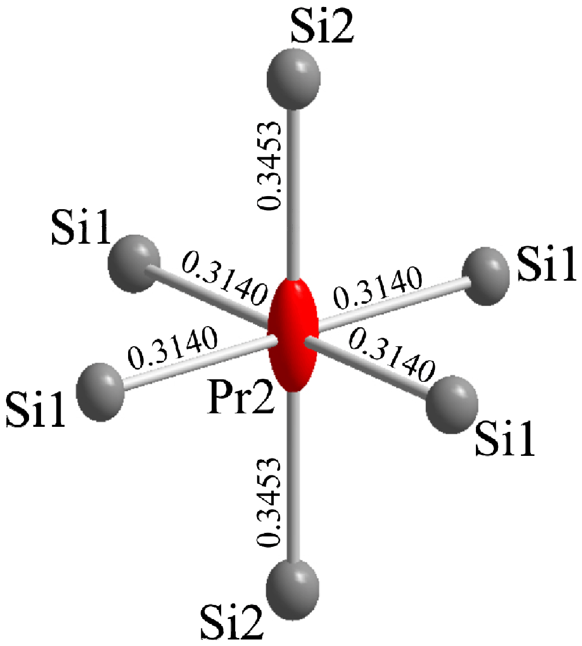

Fig. 3 Selected interatomic distances for the site Pr2 in Pr_5Si_3 (the displacement ellipsoids of the atoms are shown with 99 % probability level).

The tetragonal structure type U_3Si_2 represents an intergrowth of two simple types: W (Pearson symbol *cI*2, space group *Im*-3*m*) and AlB_2 (*hP*3, *P*6/*mmm*). The site Zr1 in the structure of Zr_3Si_2 is characterized by coordination number 17, whereas the site Zr2 exhibits coordination number 14, with a coordination polyhedron that can be regarded as a combination of a cube (formed by eight Zr1 atoms) and an octahedron (formed by two Zr2 atoms and four Si atoms). In the structure of Zr_3Si_2 the small atoms (Si) occupy the centers of trigonal prisms formed by the large atoms (Zr), but the complete coordination polyhedra are tricapped trigonal prisms (the rectangular faces of the prism are capped by one Si and two Zr atoms). The Si atoms are bonded into pairs with $\delta_{Si\text{-}Si}$ = 0.2464(6) nm. According to [30], the structure types Zr_3Al_2, Mo_2FeB_2, U_2Pt_2Sn, and Sr_2Pb_3 are related to U_3Si_2.

Most of the binary compounds that form in the Pr–Si and Zr–Si systems have trigonal-prismatic coordination of the silicon atoms. Examples are Pr_5Si_3 (structure type Cr_5B_3), Pr_3Si_2 (U_3Si_2), Pr_5Si_4 (Zr_5Si_4), PrSi (FeB), $Pr_2Si_{2.72}$ (V_2B_3), both compounds $PrSi_{2-x}$ (α-$ThSi_2$ and α-$GdSi_2$), Zr_5Si_3 (Mn_5Si_3), Zr_3Si_2 (U_3Si_2), Zr_5Si_4 (Zr_5Si_4), both modifications of ZrSi (TlI and FeB), and $ZrSi_2$ ($ZrSi_2$). From Fig. 4 one can see that in both Pr_5Si_3 and Zr_3Si_2 the trigonal prisms are distorted (slightly elongated along the [001] direction, the ratio of the height of the prism to the average value of the edges of the triangular faces $h/w = 0.4062/0.4014 = 1.012$ for Pr_5Si_3 and $0.3706/0.3631 = 1.021$ for Zr_3Si_2). The deformation is caused by bonding within the pairs of Si atoms in both structures. It is interesting to note that the compound Zr_2Si crystallizes with the structure type $CuAl_2$, which is the parent type of one of the two fragments composing the Cr_5B_3 structure adopted by Pr_5Si_3. A common feature for these structures is the coordination of the smaller atoms in the form of bicapped square antiprisms. Selected distances of the antiprisms in the Pr_5Si_3 and Zr_2Si compounds are shown in Fig. 5. The antiprisms are compressed along the [001] direction, the ratio of the height of the antiprism to the edge of the base $h/w = 0.2844/0.4079 = 0.697$ for Pr_5Si_3 and $0.2686/0.3467 = 0.775$ for Zr_2Si.

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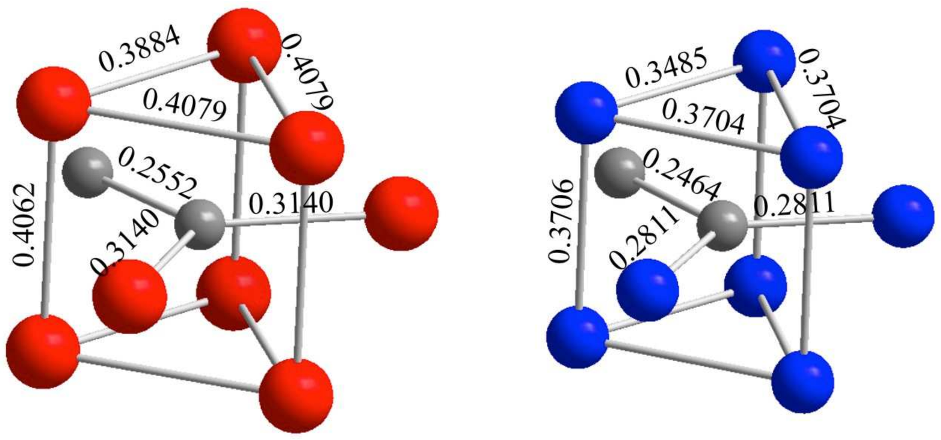
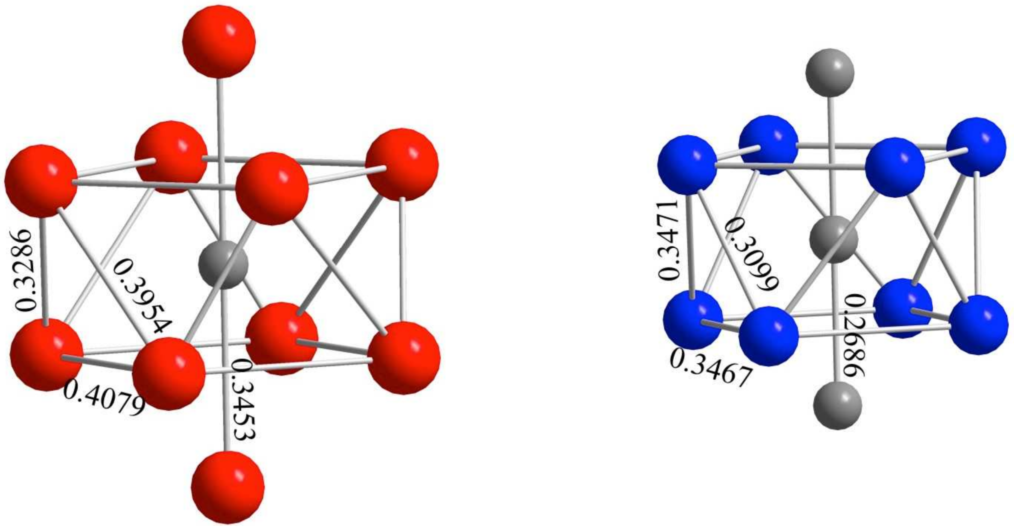


(a) (b)

Fig. 4 Trigonal-prismatic coordination of the Si atoms in the structures of Pr_5Si_3 (structure type Cr_5B_3) (a) and Zr_3Si_2 (U_3Si_2) (b).



(a) (b)

Fig. 5 Bicapped antiprismatic coordination of the Si atoms in the structures of Pr_5Si_3 (structure type Cr_5B_3) (a) and Zr_2Si ($CuAl_2$) (b).

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