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CRYSTAL STRUCTURE OF THE TERNARY COMPOUND $ErRe_{0.25}Ge_2$

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Abstract. An alloy of nominal composition $Er_{30.8}Re_{7.7}Ge_{61.5}$ was synthesized by arc melting and investigated by X-ray powder diffraction. A new ternary germanide of approximate composition $ErRe_{0.25}Ge_2$ was found, which adopts the structure type $CeNiSi_2$ (Pearson symbol *oS*16, space group *Cmcm*, $a = 4.0997(4)$, $b = 15.7348(18)$, $c = 3.9921(5)$ Å, $R_B = 0.0355$, refined composition $ErRe_{0.23(2)}Ge_2$, for the as-cast alloy; $a = 4.1117(3)$, $b = 15.6846(15)$, $c = 4.0184(3)$ Å, $R_B = 0.0420$, refined composition $ErRe_{0.28(2)}Ge_2$, after annealing at 1073 K). The coordination polyhedron of the Er atoms has 21 vertexes (hexagonal prism with nine additional atoms), that of the Re atoms is a bicapped square antiprism and the two crystallographically independent Ge atoms center tricapped trigonal prisms and cuboctahedra. The crystal structure contains layers of trigonal prisms (characteristic of the structure type AlB_2) and square antiprisms (characteristic of the structure types $BaAl_4$ and $CeAl_2Ga_2$), which alternate along the crystallographic direction [010]. The polyhedron surrounding the site partly occupied by the transition metal atoms is compared with the corresponding polyhedra in closely related structures.

Keywords: erbium, rhenium, germanium, intermetallic compound, X-ray powder diffraction, crystal structure.

1. Introduction

Among the *R*–*T*–*M* systems, where *R* is a rare earth, *T* – a *d*-element of group VII (Mn or Re), and *M* – a *p*-element of group IV, ternary compounds with $CeNiSi_2$-type structure (Pearson symbol *oS*16, space group *Cmcm*, Wyckoff sequence c^4) [1] are known in the systems *R*–Mn–Si (*R* = Pr, Er, Tm, Lu), *R*–Mn–Ge (*R* = Nd, Sm, Gd-Tm, Lu), *R*–Mn–Sn (*R* = La-Nd, Sm, Gd-Tm), *R*–Re–Ge (*R* = Gd, Ho, Lu) [2-10]. The structure type $TbFeSi_2$ (*oS*16, $Cmcm - c^4$) is closely related to the $CeNiSi_2$ type [11], the difference between the two types being in the distribution of elements over two of the four atom sites. Representatives of the $TbFeSi_2$ type have been reported in several *R*–Mn–Si systems (*R* = La, Ce-Nd, Sm) [12, 13]. The structure type $TbFeSi_2$ also has quaternary representatives in *R*–Mn–*T*–*M* systems where *T* is a *d*-element, and *M* is a *p*-element of group IV: $RMnPd_{0.5}Si_{1.5}$ (*R* = La, Ce), $RMnPt_{0.5}Si_{1.5}$ (*R* = La, Ce, Pr), $RMnCu_{0.5}Si_{1.5}$ (*R* = La, Ce-Nd), $RMnNi_{0.5}Ge_{1.5}$ (*R* = La, Ce-Nd), $RMnPd_{0.5}Ge_{1.5}$ (*R* = La, Ce-Nd), $RMnPt_{0.5}Ge_{1.5}$ (*R* = La), $RMnCu_{0.5}Ge_{1.5}$ (*R* = Nd, Sm) [14, 15]. The structure type $LaMnCu_{0.5}Ge_{1.5}$ (*oS*16, $Cmcm - c^4$) [16] is a quaternary variant of the types $CeNiSi_2$ and $TbFeSi_2$, where one of the atom sites is occupied by a statistical mixture of Cu and Ge atoms. This structure type also forms in related systems with Ce, Pr and Nd [16].

The peculiarity of the majority of the compounds that crystallize in the structure type $CeNiSi_2$ is their off-stoichiometric composition, which corresponds to partial occupation of one of the atom sites by transition metal atoms. The compound known to have the highest amount of vacancies is $TmMn_{0.02}Sn_2$, whereas in $RMnSi_2$ (*R* = Er, Tm, Lu) all the positions are fully occupied. It is interesting to note that the binary system Er–Ge contains an off-stoichiometric compound, $ErGe_{2.16}$, the structure type (*oS*16, $Cmcm - c^4$) of which is also related to the $CeNiSi_2$ type [17].

The aim of this paper was the investigation of the crystal structure of a new ternary representative of the structure type $CeNiSi_2$ discovered in the system Er–Re–Ge.

2. Experimental

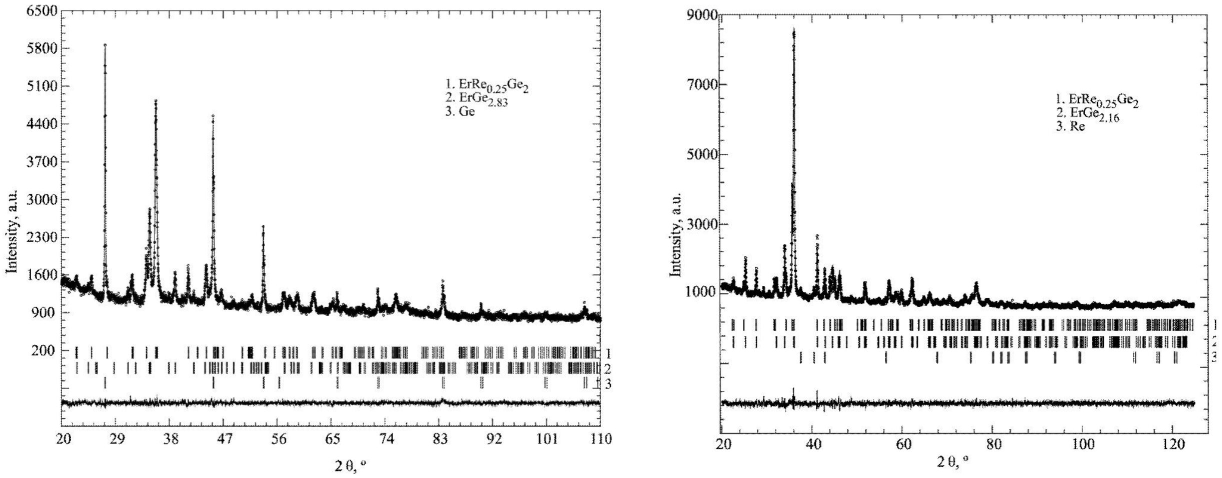
Er–Re–Ge alloys were synthesized from the elements (purity ≥ 99.7 wt %) by arc melting on a water-cooled copper bottom under a purified (using Ti as a getter) argon atmosphere with a tungsten electrode. The weight losses during the preparation of the samples were about 3 % of the total mass, which was 1 g for each alloy. Part of the alloys were annealed at 1073 K for 2 months in a quartz tube under vacuum and subsequently quenched in cold water.

Table 1

Experimental details and crystallographic data for the individual phases in the as-cast alloy of nominal composition $Er_{30.8}Re_{7.7}Ge_{61.5}$

Phase		$ErRe_{0.23(2)}Ge_2$	$ErGe_{2.83}$	Ge
Phase content, wt %		52.5(8)	22.5(7)	25.0(3)
Structure type		$CeNiSi_2$	$DyGe_3$	C diamond
Pearson symbol		*oS*16	*oS*16	*cF*8
Space group		*Cmcm*	*Cmcm*	*Fd*-3*m*
Cell parameters, Å:	*a*	4.0997(4)	4.0096(12)	5.65691(9)
	b	15.7348(18)	20.597(6)	–
	c	3.9921(5)	3.8869(10)	–
Cell volume *V*, $Å^3$		257.53(5)	320.95(2)	181.025(5)
Density D_X, g cm^{-3}		9.146	8.573	5.327
Texture parameter *G*, [direction]		0.959(6), [010]	0.975(4), [010]	0.999(5), [111]
Diffractometer		HZG-4a		
Radiation		Cu *K*α		
scanning range 2*θ*, °, step, °, time of scanning at a point, s		20-110, 0.02, 18		
Profile parameters:	*U*	0.86(14)	0.36(7)	0.041(6)
	V	-0.48(12)	-0.039(1)	-0.021(6)
	W	0.13(2)	0.033(8)	0.013(1)
Mixing parameter	η	0.803(26)	0.909(7)	0.908(26)
Asymmetry parameter	P_1	0.015(14)	0.025(7)	0.038(6)
Reliability factors:	R_B	0.0355	0.0633	0.0456
	R_F	0.0403	0.0668	0.0413
	R_p[a]	0.0282		
	R_{wp}[a]	0.0358		
	c^2	1.38		

Note: [a]without correction for background.



a) b)

Fig. 1. Experimental (dots), calculated (continuous line) and difference (continuous line at the bottom of the figures) diffractograms of the as-cast (a) and annealed (b) samples $Er_{30.8}Re_{7.7}Ge_{61.5}$ (Cu *K*α radiation). Vertical lines show the positions of the reflections *hkl* of the ternary compound $ErRe_{0.25}Ge_2$, binary compound $ErGe_{2.83}$ and Ge (a), of the ternary compound $ErRe_{0.25}Ge_2$, binary compound $ErGe_{2.16}$ and Re (b)

Phase analysis was carried out on X-ray diffraction data collected on a powder diffractometer DRON-2M (Fe *K*α radiation, Bragg-Brentano geometry, scintillation detector). The as-cast sample of nominal composition $Er_{30.8}Re_{7.7}Ge_{61.5}$ ($ErRe_{0.25}Ge_2$) contained as majority phase the ternary compound $ErRe_{0.25}Ge_2$ (structure type $CeNiSi_2$), but also the binary phase $ErGe_{2.83}$ ($DyGe_3$, *oS*16, *Cmcm* – *c*^{4}) and elementary Ge (C diamond, *cF*8, *Fd*-3*m* – *a*). The annealed alloy of the same composition also contained the ternary compound $ErRe_{0.25}Ge_2$, in this case accompanied by the majority phase $ErGe_{2.16}$ ($ErGe_{2.16}$, *oS*16, *Cmcm* – *c*^{4}) and small amounts of elementary Re (Mg, *hP*2, *P*6$_3$*/mmc* – *c*).

The structural analysis was carried out on X-ray diffraction data collected on a powder diffractometer HZG-4a (Cu *K*α radiation, Bragg-Brentano geometry, scintillation detector).

The profile parameters and structural parameters were refined using the FullProf Suite software package [18]. The binary phase $ErGe_{2.83}$ and Ge were identified as admixtures in the as-cast sample in the amounts of 22.5(7) and 25.0(3) wt %, respectively. All the phases considered in the refinement were modeled with individual scale factors, unit cell parameters, profile and preferred orientation parameters. For the main phase four atomic coordinates, three displacement parameters and one occupation parameter were refined. In total 36 parameters were allowed to vary in the final cycle of the refinement. The annealed sample also contained three phases: $ErGe_{2.16}$ (68.7(9) wt %), $ErRe_{0.25}Ge_2$ (27.2(8) wt %), and Re (4.1(1) wt %). The algorithm of the refinement was analogous to that described above: three scale factors, eight unit-cell, fifteen profile parameters and three parameters of preferred orientation. Four atomic coordinates, three displacement parameters and one occupation parameter were refined for the $ErRe_{0.25}Ge_2$ compound, so that in total 37 parameters were included in the final cycle of refinement. The isotropic displacement parameters of the Ge atoms occupying two different sites in the structure of the compound $ErRe_{0.25}Ge_2$ were constrained and refined as one parameter. Atom coordinates of $ErGe_{2.16}$ were taken from [17]. The background was refined using the Fourier filtering technique. Experimental details and crystallographic data for the individual phases in the as-cast and annealed $Er_{30.8}Re_{7.7}Ge_{61.5}$ alloys are listed in Tables 1 and 2, respectively. Experimental, theoretical and difference diffractograms are shown in Fig. 1.

Table 2

Experimental details and crystallographic data for the individual phases in the alloy of nominal composition $Er_{30.8}Re_{7.7}Ge_{61.5}$ annealed at 1073 K

Phase		$ErGe_{2.16}$	$ErRe_{0.28(2)}Ge_2$	Re
Phase content, wt %		68.7(9)	27.2(8)	4.1(1)
Structure type		$ErGe_{2.16}$	$CeNiSi_2$	Mg
Pearson symbol		*oS*16	*oS*16	*hP*2
Space group		*Cmcm*	*Cmcm*	*P*6$_3$*/mmc*
Cell parameters, Å:	*a*	4.0626(2)	4.1117(3)	2.7656(3)
	b	15.8235(8)	15.6846(15)	-
	c	3.9293(2)	4.0184(3)	4.458(1)
Cell volume *V*, Å^3		252.60(2)	259.15(4)	29.532(8)
Density D_X, g cm^{-3}		8.798	9.337	20.940
Texture parameter *G*, [direction]		0.945(4), [010]	0.998(9), [010]	0.995(15), [001]
Diffractometer		HZG-4a		
Radiation		Cu *K*α		
Interval of scanning 2*θ*, °, step, °, time of scanning in the point, s		20-125, 0.02, 18		
Profile parameters:	*U*	0.87(7)	0.25(7)	0.95(3)
	V	-0.030(5)	-0.09(5)	-0.98(4)
	W	0.059(9)	0.02(1)	0.26(11)
Mixing parameter	*η*	0.59(2)	0.91(5)	0.78(9)
Asymmetry parameter	P_1	-0.008(4)	0.015(2)	0.11(9)
Reliability factors:	R_B	0.0314	0.0420	0.0410
	R_F	0.0222	0.0306	0.0290
	R_p [a]	0.0325		
	R_{wp} [a]	0.0341		
	c^2	1.50		

Note: [a]without correction for background.

3. Results and Discussion

The ternary compound $ErRe_{0.25}Ge_2$ crystallizes in the orthorhombic structure type $CeNiSi_2$: space group *Cmcm*, Pearson symbol *oS*16, $a = 4.0997(4)$, $b = 15.7348(18)$, $c = 3.9921(5)$ Å, $R_B = 0.0355$, $R_F = 0.0403$, $c^2 = 1.38$, refined composition $ErRe_{0.23(2)}Ge_2$ (as-cast alloy); $a = 4.1117(3)$, $b = 15.6846(15)$, $c = 4.0184(3)$ Å, $R_B = 0.0420$, $R_F = 0.0306$, $c^2 = 1.50$, refined composition $ErRe_{0.28(2)}Ge_2$ (alloy annealed at 1073 K). The refined atomic coordinates, site occupancies and isotropic displacement parameters for the compound $ErRe_{0.25}Ge_2$ are listed in Table 3. Two of the four atom sites, all in Wyckoff positions 4*c*, are occupied by Ge atoms, whereas the two other sites are occupied by Er and Re atoms, respectively. The site of the rhenium atoms is approximately occupied to 25 %, so that the unit cell on the average contains thirteen atoms (three of four possible Re positions being vacant). It may be noted that the refined occupation of this site is slightly larger for the annealed alloy than for the as-cast alloy.

The coordination polyhedron of the Er atoms has 21 vertexes (hexagonal prism with nine additional atoms) – $\underline{Er}Ge_{10}Re_5Er_6$, whereas that of the Re atoms is a bicapped square antiprism – $\underline{Re}Ge_5Er_5$, where the Ge and Er atoms form two interpenetrating square pyramids. The Ge atoms are surrounded by tricapped trigonal prisms or cubo-octahedra of compositions $\underline{Ge1}Ge_2ReEr_6$ and $\underline{Ge2}Ge_4Re_4Er_4$, respectively. Interatomic distances and coordination numbers of the atoms in the structure of $ErRe_{0.25}Ge_2$ are presented in Table 4; Fig. 2 shows the content of one unit cell and the coordination polyhedra of the four sites.

Table 3

Atomic coordinates, isotropic displacement parameters and occupation parameters for $ErRe_{0.25}Ge_2$

Atom	Wyck.	*x*	y^a	y^b	*z*	$B_{iso}{}^a$, Å^2	$B_{iso}{}^b$, Å^2	Occ.^{a}	Occ.^{b}
Er	4*c*	0	0.3980(4)	0.3998(6)	¼	0.35(1)	0.56(2)	1	1
Re	4*c*	0	0.1950(11)	0.1924(12)	¼	0.86(4)	0.55(4)	0.23(2)	0.28(2)
Ge1	4*c*	0	0.0568(7)	0.0536(11)	¼	1.31(2)	0.93(3)	1	1
Ge2	4*c*	0	0.7552(6)	0.7518(10)	¼	1.31(2)	0.93(3)	1	1

Notes: ^{a}as-cast alloy; ^{b}alloy annealed at 1073 K.

Table 4

Interatomic distances and coordination numbers of the atoms in the structure of $ErRe_{0.25}Ge_2$

Atoms		d^a, Å	d^b, Å	CN
Er	– 4 Ge1	2.948(3)	2.966(5)	21
	– 2 Ge2	3.041(8)	3.101(14)	
	– 2 Ge2	3.130(9)	3.113(14)	
	– 1 Re	3.194(18)	3.253(15)	
	– 4 Re	3.214(8)	3.218(5)	
	– 2 Ge1	3.232(10)	3.169(15)	
	– 2 Er	3.780(8)	3.730(11)	
	– 2 Er	3.9920(5)	4.0184(3)	
	– 2 Er	4.0997(4)	4.1117(3)	
Re	– 2 Ge2	2.144(7)	2.192(10)	10
	– 1 Ge1	2.175(15)	2.177(25)	
	– 2 Ge2	2.258(8)	2.257(1)	
	– 1 Er	3.194(18)	3.253(15)	
	– 4 Er	3.214(8)	3.218(5)	
Ge1	– 1 Re	2.175(15)	2.177(25)	9
	– 2 Ge1	2.679(10)	2.620(16)	
	– 4 Er	2.948(3)	2.966(5)	
	– 2 Er	3.232(10)	3.169(15)	
Ge2	– 2 Re	2.144(7)	2.192(10)	12
	– 2 Re	2.258(8)	2.257(1)	
	– 4 Ge2	2.8658(8)	2.8752(5)	
	– 2 Er	3.041(8)	3.101(14)	
	– 2 Er	3.130(9)	3.113(14)	

Notes: ^{a}as-cast alloy; ^{b}alloy annealed at 1073 K.

Table 5

Unit-cell parameters and volume for compounds with $CeNiSi_2$-type structures in *R*–Re–Ge systems

Compound	Unit-cell parameters, Å			V, Å^3	Ref.
	a	*b*	*c*		
$GdRe_{0.24\text{-}0.25}Ge_2$	4.158-4.162	16.07	4.056	271.2-271.4	[3]
$GdRe_{0.28}Ge_2$	4.1584	16.092	4.0521	271.15	[19]
$HoRe_{0.25}Ge_2$	4.128	15.78	4.028	262.3	[3]
$ErRe_{0.23(2)}Ge_2{}^a$	4.0997(4)	15.7348(18)	3.9921(5)	257.5 3(5)	This work
$ErRe_{0.28(2)}Ge_2{}^b$	4.1117(3)	15.6846(15)	4.0184(3)	259.15(4)	This work
$LuRe_{0.12}Ge_2$	4.085	15.51	3.991	253.0	[3]

Notes: ^{a}as-cast alloy; ^{b}alloy annealed at 1073 K.

Investigations of compounds isostructural to $ErRe_{0.25}Ge_2$ in *R*–Re–Ge systems have been reported earlier [3, 19]. François *et al.* [3] describe three compounds with $CeNiSi_2$-type structures in the systems with Lu, Ho and Gd. The compound with Gd revealed a small homogeneity range, whereas the other compounds displayed point compositions. The unit-cell parameters and cell volume decrease with increasing atomic number of the rare-earth elements, as expected from the decrease of the atomic radii (Table 5).

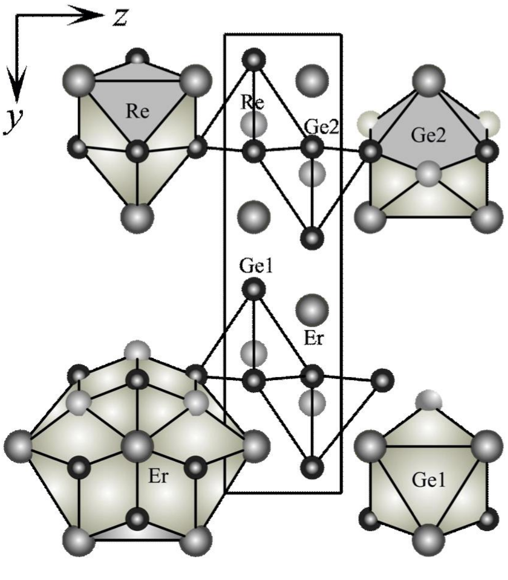


Fig. 2. Projection of the unit cell of the structure of the compound $ErRe_{0.25}Ge_2$ onto the plane *yz* and coordination polyhedra of the atoms. Layers (perpendicular to the *y*-axis) formed by square pyramids $[Ge_5]$ in part occupied by Re atoms are indicated

The structure types $ZrSi_2$ (Pearson symbol *oS*12, space group *Cmcm*, Wyckoff sequence c^3), $ErGe_{2.16}$ (*oS*16, *Cmcm* – c^4), $CeNiSi_2$ (*oS*16, *Cmcm* – c^4), $TbFeSi_2$ (*oS*16, *Cmcm* – c^4) and $LaMnCu_{0.5}Ge_{1.5}$ (*oS*16, *Cmcm* – c^4) are closely related. As can be seen from Fig. 3, the structure of the binary germanide $ErGe_{2.16}$ can be deduced from the structure of the binary silicide $ZrSi_2$ by the inclusion of additional *p*-element atoms into part of the square-antiprismatic voids. The structure of the compound $ErRe_{0.25}Ge_2$ ($CeNiSi_2$ type) can be obtained by replacing the *p*-element atoms in the partly occupied Wyckoff position 4*c* by *d*-element atoms. The redistribution of *p*- and *d*-element atoms in two of the four atom sites leads to the structure type $TbFeSi_2$. In the structure type $LaMnCu_{0.5}Ge_{1.5}$ the four atom sites are occupied by different kinds of atoms (one of them by a statistical mixture of *d*-(Cu) and *p*-element atoms). Accordingly the structure types $CeNiSi_2$ and $TbFeSi_2$ are ternary variants of the structure type $ErGe_{2.16}$, and the structure type $LaMnCu_{0.5}Ge_{1.5}$ is a quaternary variant of the three types.

As described above, in the *R*–*T*–*M* systems, where *R* is a rare earth, *T* is a *d*-element, and *M* is a *p*-element, the structure type $CeNiSi_2$ is very often formed at an off-stoichiometric composition. The atoms of the *T*-component are located at the centers square antiprisms formed by *p*- and *f*-elements. The occupancy of these sites depends on the periodic number of the rare-earth element and on the nature of the *T*- and *M*-components. The *R* atoms, which occupy one half of the vertexes of the square antiprism (forming one of the square faces), reduce the volume of the polyhedron with increasing periodic number of the rare-earth element. If the four other vertexes of the square antiprism are occupied by atoms of a *M*-component with sufficiently pronounced non-metallic character, such as germanium, reduction of the interatomic distances with partial electron density localization is observed within the polyhedron.

The shortening of the interatomic distances leads to deformation of the square antiprism surrounding the site occupied by *T*- or *M*-atoms. One of the square faces (composition [*R*4]) of the square antiprism is significantly larger than the other one (composition [*X*4] or [*M*4]), which undergoes orthorhombic deformation. A *T*- or *M*-component atom is located above the large face, whereas an *R* atom caps the smaller face, at a longer distance from the central atom than the *M* and *T* atoms. The resulting bicapped square antiprism can be divided into two interpenetrating square pyramids: a larger one of

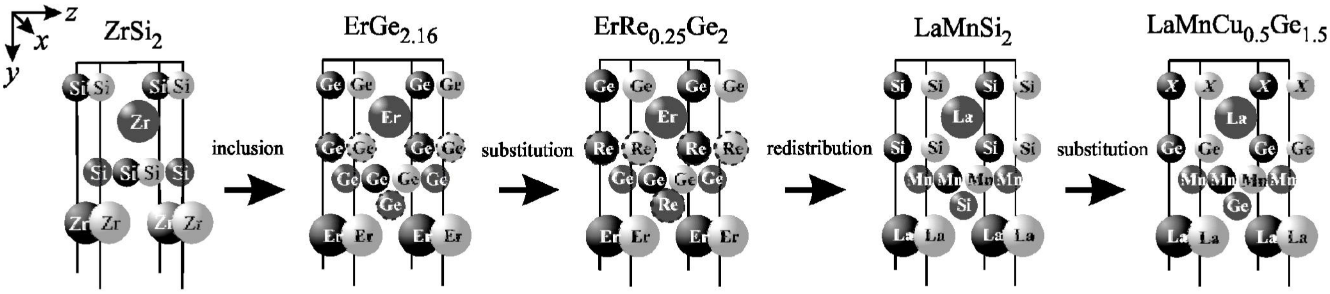
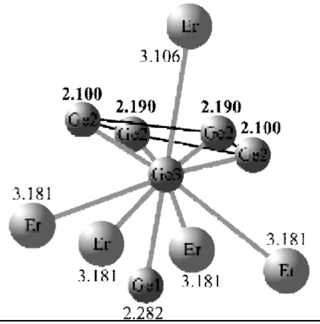
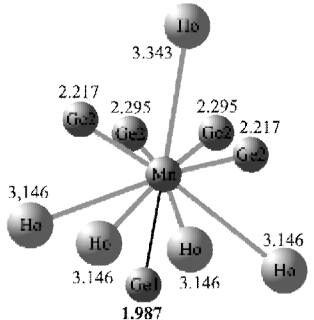
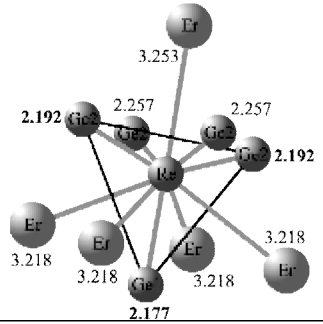


Fig. 3. The structures of $ZrSi_2$, $ErGe_{2.16}$, $ErRe_{0.25}Ge_2$ ($CeNiSi_2$ type), $LaMnSi_2$ ($TbFeSi_2$ type), and $LaMnCu_{0.5}Ge_{1.5}$. Part of the unit cell ($0 < y < 0.4$) is shown

Table 6

Peculiarities of the coordination polyhedron of the "square-antiprismatic" site in different structures of the $CeNiSi_2$ structure type family

<table>
<tr><td colspan="3">$ErGe_{2.16}$ (own structure type) [17]</td><td colspan="3">$HoMn_{0.33}Ge_2$ ($CeNiSi_2$ type) [5]</td><td colspan="3">$ErRe_{0.28}Ge_2$ ($CeNiSi_2$ type)</td></tr>
<tr><td colspan="3">$a = 4.039$, $b = 15.662$, $c = 3.9093$ Å</td><td colspan="3">$a = 4.091$, $b = 15.770$, $c = 3.979$ Å</td><td colspan="3">$a = 4.1117$, $b = 15.6846$, $c = 4.0184$ Å</td></tr>
<tr><td colspan="2">Atoms</td><td>d, Å</td><td colspan="2">Atoms</td><td>d, Å</td><td colspan="2">Atoms</td><td>d, Å</td></tr>
<tr><td>Ge3[a]</td><td>– 2 Ge2
– 2 Ge2
– 1 Ge1
– 1 Er
– 4 Er</td><td>2.100
2.190
2.282
3.106
3.181</td><td>Mn[a]</td><td>– 1 Ge1
– 2 Ge2
– 2 Ge2
– 4 Ho
– 1 Ho</td><td>1.987
2.217
2.295
3.146
3.343</td><td>Re[a]</td><td>– 1 Ge1
– 2 Ge2
– 2 Ge2
– 4 Er
– 1 Er</td><td>2,177
2,192
2,257
3,218
3,253</td></tr>
<tr><td colspan="3">
</td><td colspan="3">
</td><td colspan="3">
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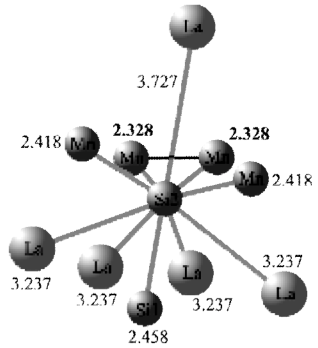
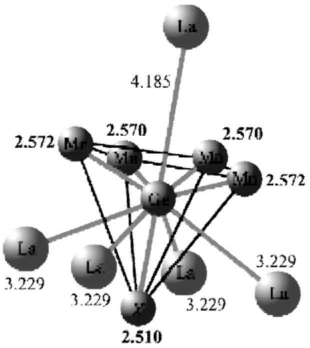
<table>
<tr><td colspan="3">$LaMnSi_2$ ($TbFeSi_2$ type) [12]</td><td colspan="3">$LaMnCu_{0.5}Ge_{1.5}$ (own structure type) [16]</td></tr>
<tr><td colspan="3">$a = 4.191$, $b = 17.68$, $c = 4.073$ Å</td><td colspan="3">$a = 4.203$, $b = 18.266$, $c = 4.2294$ Å</td></tr>
<tr><td colspan="2">Atoms</td><td>d, Å</td><td colspan="2">Atoms</td><td>d, Å</td></tr>
<tr><td>Si2</td><td>– 2 Mn
– 2 Mn
– 1 Si1
– 4 La
– 1 La</td><td>2.328
2.418
2.458
3.237
3.727</td><td>Ge</td><td>– 1 X[b]
– 2 Mn
– 2 Mn
– 4 La
– 1 La</td><td>2.510
2.570
2.572
3.229
4.185</td></tr>
<tr><td colspan="3">
</td><td colspan="3">
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Notes: [a]partly occupied position; [b]$X = 0.5$ Cu + 0.5 Ge.

composition [R_5], and a smaller one of composition [M_5], [T_4M] or [T_5]. If we consider the coordination polyhedron of the Ge atoms in the defect position in the structure of the binary compound $ErGe_{2.16}$, the atoms at the shortest distances to the central atom form a slightly deformed square within the square pyramid of composition [Ge_5] (Table 6). The shortest distance in the structure of the compound $HoMn_{0.33}Ge_2$ ($CeNiSi_2$ type) connects the central Mn atom to the Ge atom at the vertex of the square pyramid of composition [Ge_5]. In the compound $ErRe_{0.25}Ge_2$ the nearest Re atoms form a triangle of composition [Ge_3]. In the structure of the compound $LaMnSi_2$ ($TbFeSi_2$ type) the square pyramid has the composition [Mn_4Si] and two of the Mn atoms are situated slightly closer to the central Si atom. Only in the structure type $LaMnCu_{0.5}Ge_{1.5}$ the square pyramids of compositions [Mn_4Cu] and [Mn_4Ge] around the Ge atoms are more or less ideal.

The crystal structure of the compound $ErRe_{0.25}Ge_2$ ($CeNiSi_2$ type) contains, in addition to layers of square antiprisms (characteristic of the $BaAl_4$ type or its ordered variant $CeAl_2Ga_2$), layers of trigonal prisms (characteristic of the AlB_2 type), two kinds alternating along the *y*-axis in the ratio 1:1. The structure types $TmLi_{1-x}Ge_2$, $NdRuSi_2$, $ErGe_{2.16}$, $TbFeSi_2$, $LaMnCu_{0.5}Ge_{1.5}$, $CeRhGe_2$, $NdNiGa_2$, $Sr_2Pd_3P_3$, $Ce_3Ni_2Si_8$, Eu_3Ga_8, $U_3Ni_4Si_4$, and $Sr_4Pd_5P_5$ are built up from similar layers, but in different ratios and/or stacking sequences (Fig. 4) [1,11,16,17,20-29]. In the monoclinic derivatives of the $CeNiSi_2$-type structure, $Li_{1-x}Ge_2$ and $NdRuSi_2$, only two layers, AlB_2 (A) and $BaAl_4$ (B), alternate along the longest unit-cell parameter (*z*-axis). The two types differ by the degree of deformation. In the structure type $CeNiSi_2$ and the related types $ErGe_{2.16}$, $TbFeSi_2$, $LaMnCu_{0.5}Ge_{1.5}$, $CeRhGe_2$, and $NdNiGa_2$ the stacking sequence is identical but the longest unit-cell parameter (*y*- or *z*-axis) contains four layers: AlB_2 (A) – $BaAl_4$ (B) – AlB_2 (A) – $BaAl_4$ (B). The structure type $CeRhGe_2$ is a derivative of the $CeNiSi_2$ type with an orthorhombic primitive lattice, whereas the structure type $NdNiGa_2$ contains differently cut $BaAl_4$-type fragments (B’). Other combinations of layers lead to an increase of the unit-cell parameter (*y*- or *z*-axis) and formation of the structure types Eu_3Ga_8, $U_3Ni_4Si_4$, $Ce_3Ni_2Si_8$, and $Sr_2Pd_3P_3$.

The structure type $U_3Ni_4Si_4$ is a ternary variant of the structure type Eu_3Ga_8. In $Sr_4Pd_5P_5$ the layer sequence $(AlB_2)_3$ (AAA) – $BaAl_4$ (B) – $(AlB_2)_3$ (AAA) – $BaAl_4$ (B) leads to an increase of the unit-cell parameter *b*; the structure also shows doubling of the unit-cell parameter *c*. Replacing the $BaAl_4$ (B) layers by layers characteristic of the structure type CaF_2 (C) in $CeNiSi_2$, the structure type $ZrSi_2$ is formed. There exist also other structure types, such as Tb_4FeGe_8 [30], where the vacant positions are ordered, resulting in the formation of superstructures of the $CeNiSi_2$-type.

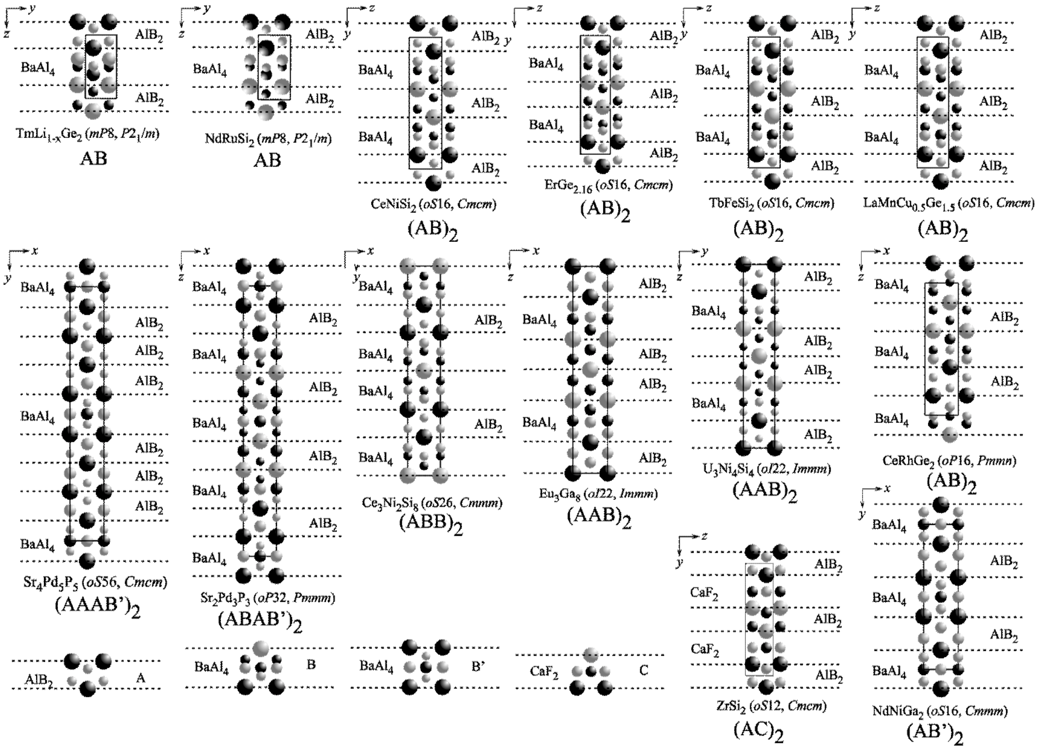

Fig 4. Structure types formed by slabs of the AlB_2, $BaAl_4$ and CaF_2 types

4. Conclusions

The crystal structure of the new germanide $ErRe_{0.25}Ge_2$ belongs to the $CeNiSi_2$ type (Pearson symbol *oS*16, space group *Cmcm*). The coordination polyhedra of the atoms are as follows: for Er a 21-vertex polyhedron that can be described as a hexagonal prism with nine additional atoms, for Re – a square antiprism with two additional atoms, for Ge – a trigonal prism with three additional atoms or a cuboctahedron.

The $CeNiSi_2$-type compounds that form in the systems $R–T–M$ (R = rare-earth metal, T = d-element, M = p-element) are often deficient with respect to the T-component. Deficiency leads to deformation of the coordination polyhedron.

The crystal structure of the compound $ErRe_{0.25}Ge_2$ contains layers of trigonal prisms (characteristic of the structure type AlB_2) and layers of square antiprisms (characteristic of the structure type $BaAl_4$ or $CeAl_2Ga_2$), which alternate along the crystallographic direction [010]. The structure types $TmLi_{1-x}Ge_2$, $NdRuSi_2$, $ErGe_{2.16}$, $TbFeSi_2$, $LaMnCu_{0.5}Ge_{1.5}$, $CeRhGe_2$, $NdNiGa_2$, $Sr_2Pd_3P_3$, $Ce_3Ni_2Si_8$, Eu_3Ga_8, $U_3Ni_4Si_4$, and $Sr_4Pd_5P_5$ are built up from similar fragments.

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КРИСТАЛІЧНА СТРУКТУРА ТЕРНАРНОЇ СПОЛУКИ $ErRe_{0,25}Ge_2$

Анотація. *Зразок вихідного складу* $Er_{30,8}Re_{7,7}Ge_{61,5}$ *синтезовано методом електродугової плавки та досліджено рентгенівським дифракційним методом порошку. Знайдено новий тернарний германід* $ErRe_{0,25}Ge_2$*, кристалічна структура якого належить до типу* $CeNiSi_2$ *(символ Пірсона* *oS16*, *просторова група* *Cmcm*, $a = 4,0997(4)$, $b = 15,7348(18)$, $c = 3,9921(5)$ Å, $R_B = 0,0355$, *уточнений склад* $ErRe_{0,23(2)}Ge_2$*, литий сплав;* $a = 4,1117(3)$, $b = 15,6846(15)$, $c = 4,0184(3)$ Å, $R_B = 0,0420$, *уточнений склад* $ErRe_{0,28(2)}Ge_2$*, зразок, відпалений при 800°C). Координаційним многогранником атомів Er є 21-вершинник (гексагональна призма з дев'ятьма додатковими атомами), атомів Re – двошапкова тетрагональна антипризма, а два кристалографічно незалежні атоми Ge центрують тришапкові тригональні призми або кубооктаедри. Кристалічна структура сполуки* $ErRe_{0,25}Ge_2$ *містить шари тригональних призм (характеристика структурного типу* AlB_2*) та тетрагональних антипризм (характеристика структурного типу* $BaAl_4$ *чи* $CeAl_2Ga_2$*), які чергуються вздовж кристалографічного напрямку [010]. Поліедр навколо положення, частково зайнятого атомами перехідного металу, зіставлено з відповідними поліедрами в близькоспоріднених структурах.*

Ключові слова: *ербій, реній, германій, інтерметалічна сполука, рентгенівська порошкова дифракція, кристалічна структура.*