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The Structure Type $ZrAl_{0.23}Ge_{1.77}$

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The new ternary intermetallic compound $ZrAl_{0.23}Ge_{1.77}$ was observed after annealing at 600°C, and its crystal structure was determined by X-ray single-crystal diffraction. The structure (own structure type, Pearson symbol $tI32-8$, space group $I4_1/amd$, $a = 3.8013(2)$, $c = 29.893(3)$ Å, $Z = 4$) is a variant with partial positional disorder of the pseudo-binary structure type $Zr_{0.75}AlSi_{1.25}$. The structures are members of the family of linear intergrowth structures composed of AlB_2-type slabs (layers of centered trigonal prisms) and CaF_2-type slabs (layers of empty "half octahedra"), here in the ratio 1:2. The structure of $ZrAl_{0.23}Ge_{1.77}$ is characterized by statistical occupation by Al and Ge of one of the sites forming the CaF_2-type slabs and positional disorder of the Ge atoms that form *zig-zag* chains along the crystallographic direction [100].

Keywords: Zirconium; Aluminum; Germanium; X-Ray single-crystal diffraction; Ternary compound; Crystal structure; Intergrowth structure.

Introduction

During an investigation of the phase diagram of the ternary system Zr–Al–Ge at 600°C we found four ternary compounds and reported the crystal structures of three of them: $ZrAl_{2.52}Ge_{0.48}$ (structure type (ST) $TiAl_3$, Pearson symbol (PS) $tI8$, space group (SG) $I4/mmm$: $a = 3.92395$, $c = 9.0476$ Å) [1], Zr_5AlGe_3 (ST Hf_5CuSn_3, PS $hP18$, SG $P6_3/mcm$, $a = 8.104$, $c = 5.654$ Å) [2], and $Zr_5Al_{2.70}Ge_{0.30}$ (ST Nb_5SiSn_2, PS $tI32$, SG $I4/mcm$, $a = 11.0145$, $c = 5.3921$ Å) [3]. $ZrAl_{2.52}Ge_{0.48}$ is a member of the family of cubic close-packed structures, which derive from the face-centered cubic structure type Cu. Zr_5AlGe_3 represents a filled-up Nowotny phase, and derives from the binary structure type Mn_5Si_3, whereas the structure of $Zr_5Al_{2.70}Ge_{0.30}$ adopts a ternary variant of the structure type W_5Si_3, and probably forms *via* stabilization at lower temperatures of the substitutional solid solution based on the high-temperature modification of Zr_5Al_3 (> 1000°C). In all these structures a tendency towards ordering of Al and Ge atoms was observed.

The aim of the present work was to determine the crystal structure of the fourth ternary compound, $ZrAl_{0.23}Ge_{1.77}$. In the related systems Ti–Al–{Si, Ge} and Zr–Al–Si, ternary phases adopting the tetragonal structure type $Zr_{0.75}AlSi_{1.25}$ (PS $tI24$, SG $I4_1/amd$) have been reported [4]. The crystallographic data of these phases are summarized in Table 1.

Table 1

Cell parameters of ternary compounds with $Zr_{0.75}AlSi_{1.25}$-type structures (Pearson symbol $tI24$, space group $I4_1/amd$).

Compound	Cell parameters, Å		Ref.
	a	c	
$TiAl_{0.24}Si_{1.76}$	3.5788	27.132	[6]
$Ti_{0.87}Al_{0.63}Si_{1.50}$	3.57	27.15	[7]
$Zr_{0.75}AlSi_{1.25}$	3.71	29.35	[7]
$TiAl_{0.29}Ge_{1.71}$	3.6859	28.345	[8]

The structure of $Zr_{0.75}AlSi_{1.25}$ represents a pseudo-binary structure type, $(Zr_{0.75}Al_{0.25})(Si_{0.625}Al_{0.375})_2$, which has later been reported also for binary compounds such as $ScSn_2$. Considering the difficulty to distinguish Si and Al by X-ray diffraction, partial order of these two elements cannot be excluded. The structure belongs to the family of intergrowth structures that can be decomposed into slabs characteristic of the simple structure types AlB_2 and CaF_2 [5].
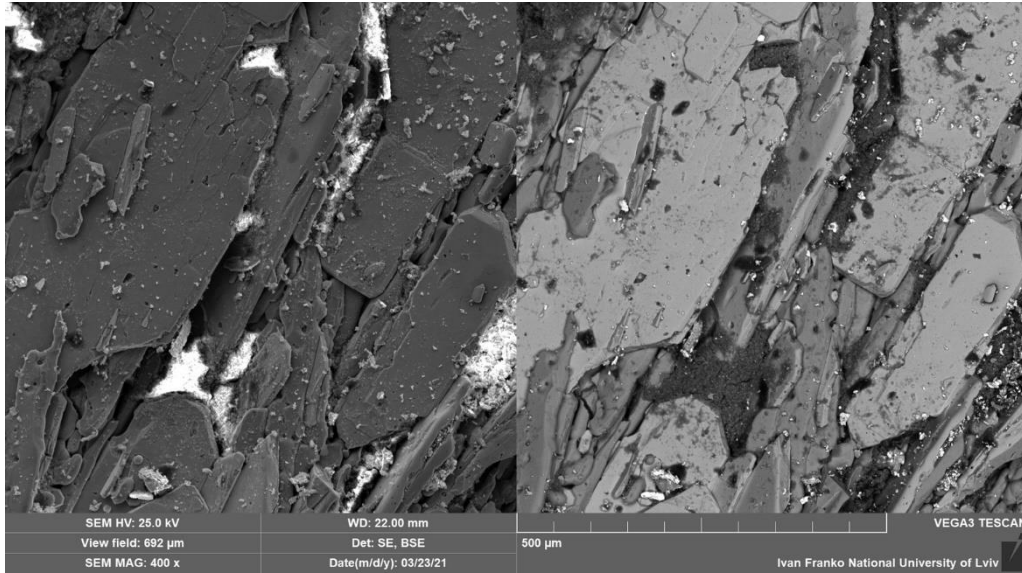
Fig. 1. Image of the surface of the sample Zr$_{33.3}$Al$_{10}$Ge$_{56.7}$ in SE and BSE modes.

I. Experimental details

An alloy of nominal composition Zr$_{33.3}$Al$_{10}$Ge$_{56.7}$ was synthesized from high-purity metals ($\geq$ 99.9 mass%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using a tungsten electrode and porous Ti as a getter. To achieve homogeneity the sample was melted twice. After the synthesis the ingot was wrapped into tantalum foil, sealed in a quartz ampoule under vacuum and annealed at 600°C for 1 month. Finally, the ampoule with the sample was quenched into cold water. The mass loss was less than 0.5 % of the total mass, which was approximately 1 g.

A plate-like single crystal was extracted from the alloy, mounted on a glass fiber, and X-ray diffraction data were collected at room temperature on a Rigaku AFC7 diffractometer, equipped with a Mercury CCD detector (graphite monochromator, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). An absorption correction was performed applying a multi-scan procedure.

The structure of the ternary compound was solved by direct methods in the centrosymmetric tetragonal space group $I4_1/amd$; the atomic positional and anisotropic displacement parameters were refined by the full-matrix least-squares method, using the program package WinCSD [9]. Experimental details and crystallographic data for ZrAl$_{0.23}$Ge$_{1.77}$ are listed in Table 2.

The composition of the ternary compound (Zr$_{0.99(2)}$Al$_{0.25(3)}$Ge$_{1.75(3)}$) was independently determined by energy-dispersive X-ray spectral analysis, performed on a scanning electron microscope TESCAN Vega3 LMU (Fig. 1), equipped with an energy dispersion X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^{N}20.

II. Results and discussion

The crystal structure of the ternary alumogermanide ZrAl$_{0.23}$Ge$_{1.77}$ represents a new structure type (Pearson

Table 2

Experimental details and crystallographic data for ZrAl$_{0.23}$Ge$_{1.77}$

Compound composition		ZrAl$_{0.23}$Ge$_{1.77}$
Formula weight		225.98
Pearson symbol		tI32
Space group		$I4_1/amd$
Cell parameters:	a, Å	3.8013(2)
	c, Å	29.893(3)
Cell volume V, Å^3		431.95(9)
Formula units per cell Z		8
Density D_X, g cm^{-3}		6.950
Absorption coefficient μ, mm^{-1}		30.16
No. of reflections: measured independent (with $F > 3\sigma(F)$)		1474 254
Reliability factor	R_{eq}	0.0392
Range of h, k, l		$-5 \leq h \leq 2$, $-5 \leq k \leq 5$, $-43 \leq l \leq 43$
θ_{max}, °		33.2
Reliability factors:	R	0.0311
	wR	0.0320
	S	1.01

symbol tI32-8, space group $I4_1/amd$), which is characterized by partial disorder of the Al and Ge atoms. Atom coordinates and displacement parameters for ZrAl$_{0.23}$Ge$_{1.77}$ are given in Table 3.

The structure is closely related to the structure type Zr$_{0.75}$AlSi$_{1.25}$ [7], which has the same space group and similar cell parameters and to which the structures of three chemically related ternary compounds belong (see Table 1). During the structure refinement, positional disorder for the Ge atoms occupying site Ge1 was evidenced by large values of the displacement parameters. The disorder was successfully modeled by splitting the site in Wyckoff position 8e into two positions shifted along [001] (sites Ge1A and Ge1B). The site occupancy of both sites was conveniently fixed at 50 %. The refined distance between neighboring positions of the split sites is 0.254(3) Å.

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Table 3

Atom coordinates and displacement parameters (Å^2) for ZrAl$_{0.23}$Ge$_{1.77}$ (PS tI32, SG $I4_1/amd$, origin choice 2, $a = 3.8013(2)$, $c = 29.893(3)$ Å, $R = 0.0311$, $wR = 0.0320$)

Site	Wyckoff position	x	y	z	B_{iso}
Zr	8e	0	1/4	0.19867(4)	0.47(3)
M [a]	4b	0	1/4	3/8	0.67(4)
Ge1A [b]	8e	0	1/4	0.02789(6)	0.35(4)
Ge1B [b]	8e	0	1/4	0.0364(1)	0.26(12)
Ge2	4a	0	3/4	1/8	0.69(3)

Site	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zr	0.34(5)	0.27(5)	0.81(4)	0	0	0
M [a]	0.50(6)	0.50(6)	1.02(9)	0	0	0
Ge1A [b]	0.39(8)	0.31(8)	0.36(6)	0	0	0
Ge1B [b]	0.3(2)	0.2(2)	0.24(12)	0	0	0
Ge2	0.51(4)	0.51(4)	1.05(7)	0	0	0

[a] $M = 0.461(9)$Al $+ 0.539(9)$Ge; [b] occ. (Ge1A) = occ. (Ge1B) = 0.5.
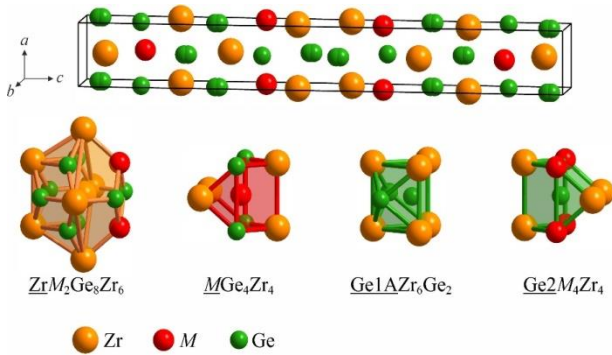
Fig. 2. Cell content and coordination polyhedra in the structure of ZrAl$_{0.23}$Ge$_{1.77}$.

The composition of the ternary alumosilicides Zr$_{0.75}$AlSi$_{1.25}$ and Ti$_{0.87}$Al$_{0.63}$Si$_{1.50}$ [7] differ from the ideal T:M ratio 1:2 (T – transition metal, M – p-element) due to the formation of statistical mixtures of Zr (or Ti) and Al atoms. At the same time, also the Si atoms are in part replaced by Al atoms. In the structure of the alumogermanide ZrAl$_{0.23}$Ge$_{1.77}$, similarly to TiAl$_{0.29}$Ge$_{1.71}$ [8], the corresponding site in Wyckoff position 8e is exclusively occupied by transition metal atoms, while Al and Ge atoms are distributed over the other sites in a partly disordered way. Statistical mixture of Al and Ge atoms was found for the site in Wyckoff position 4b, whereas the sites in 4a and 8e are occupied by Ge atoms alone. Both structures, ZrAl$_{0.23}$Ge$_{1.77}$ and TiAl$_{0.29}$Ge$_{1.71}$, are thus ternary, partially ordered variants of the pseudo-binary structure type Zr$_{0.75}$AlSi$_{1.25}$. It may be mentioned that the displacement ellipsoid of the Ge site in Wyckoff position 8e in TiAl$_{0.29}$Ge$_{1.71}$ shows a relatively high value along [001]. The cell content and coordination polyhedra of the atoms in the structure of ZrAl$_{0.23}$Ge$_{1.77}$ are shown in Fig. 2, interatomic distances and coordination numbers are listed in Table. 4.

The Zr atoms are coordinated by 16 atoms, which form a polyhedron of composition $\underline{Zr}M_2$Ge$_8$Zr$_6$. This polyhedron can be described as a cuboctahedron of composition M_2Ge$_8$Zr$_2$ with four additional Zr atoms. The atoms belonging to the closest environment of sites

Table 4

Interatomic distances (δ) within the coordination polyhedra and coordination numbers (CN) in the structure of ZrAl$_{0.23}$Ge$_{1.77}$

| Atoms		δ, Å	CN
Zr	– 4 Ge1B [a]	2.725(1)	
	(4 Ge1A [a])	(2.778(1))	
	– 2 Ge2	2.909(1)	
	– 2 M [b]	2.909(1)	
	– 2 Ge1A	3.037(2)	16
	(2 Ge1B [a])	(3.239(3))	
	– 2 Zr	3.610(1)	
	– 4 Zr	3.801(1)	
M [b]	– 4 Ge2	2.688(1)	8
	– 4 Zr	2.909(1)	
Ge1A	(1 Ge1B [a])	(0.254(3))	
	– 2 Ge1A [a]	2.528(2)	
	(2 Ge1B [a])	(2.703(2))	8
	– 4 Zr	2.778(1)	
	– 2 Zr	3.037(2)	
Ge1B	(1 Ge1A [a])	(0.254(3))	
	– 2 Ge1A	2.703(2)	
	(2 Ge1B [a])	(2.889(3))	8
	– 4 Zr	2.725(1)	
	– 2 Zr	3.239(3)	
Ge2	– 4 M [b]	2.688(1)	8
	– 4 Zr	2.909(1)	

[a] partially occupied sites; [b] $M = 0.461(9)$Al $+ 0.539(9)$Ge

M (statistical mixture of Al and Ge atoms) and Ge2 form 8-vertex polyhedra $\underline{M}$Ge$_4$Zr$_4$ and $\underline{Ge2}M_4$Zr$_4$, respectively, which are made from two mutually perpendicular trigonal prisms sharing a square face (a *gyrobifastigium*). The Ge atoms from site Ge1A are coordinated by six Zr atoms forming a trigonal prism, and two Ge atoms capping rectangular faces of the prism. The Ge atoms from site Ge1B have the same type of polyhedron, with different distribution of distances.

Contact distances are observed between Ge atoms from the sites Ge1A and Ge1B, situated near the centers of the trigonal prisms Zr$_6$ (see Fig. 3a,b), indicating strong homonuclear interaction (covalent and metallic radii for Ge are: $r_{cov} = 1.220$ Å, $r_{met} = 1.369$ Å). These atoms form
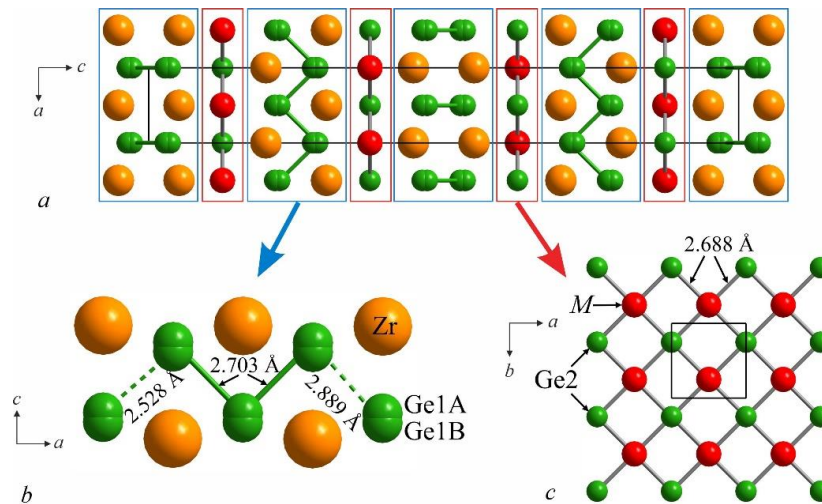
Fig. 3. Projection of the structure of ZrAl$_{0.23}$Ge$_{1.77}$ onto the (101) plane with highlighted Ge-atom *zig-zag* chains and planar square-mesh nets of Al and Ge atoms (*a*), enlarged projection of the Ge-atom *zig-zag* chain onto the (101) plane (*b*), and a planar square-mesh net of Al and Ge atoms in the (110) plane (*c*).
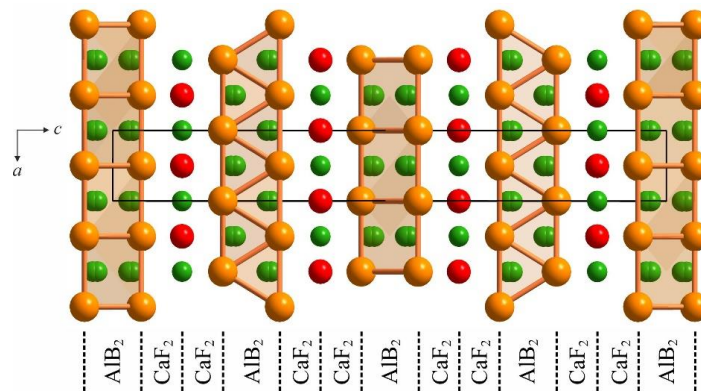
Fig. 4. Intergrowth of AlB$_2$- and CaF$_2$-type slabs in the structure of ZrAl$_{0.23}$Ge$_{1.77}$ along the crystallographic direction [001].

infinite *zig-zag* chains along [100] and [010] and the shortest "possible" distance between split positions (Ge1A-Ge1A) is only slightly longer than the distance in elementary Ge. The Ge atoms from site Ge2 and the atoms from site *M* (approximately 50 % Al + 50 % Ge) form planar square-mesh nets in the (001) plane, where interatomic distances of the same magnitude as δ(Ge1A-Ge1B) are observed (Fig. 3*c*).

The structure of ZrAl$_{0.23}$Ge$_{1.77}$ belongs to the family of linear intergrowth structures composed of AlB$_2$-type and CaF$_2$-type slabs [5]. The former can be represented by layers of fused centered trigonal prisms and the latter by layers of empty "half octahedra". In ZrAl$_{0.23}$Ge$_{1.77}$, single AlB$_2$-type layers, built from trigonal prisms centered by Ge atoms and formed by Zr atoms, alternate with two CaF$_2$-type layers, containing the sites *M* and Ge2, along the crystallographic direction [001]. Consecutive layers of trigonal prisms are rotated by 90° around [001], whereas the CaF$_2$-type layers in the double slabs are shifted with respect to each other in the (001) plane, so that a glide plane appears at the interface.

Conclusions

The new ternary compound ZrAl$_{0.23}$Ge$_{1.77}$ was synthesized and its crystal structure determined by X-ray single-crystal diffraction. The structure belongs to a new structure type, which is a ternary variant with partial positional disorder of the pseudo-binary structure type Zr$_{0.75}$AlSi$_{1.25}$. It differs from the latter by the modelling of positional disorder of the Ge atoms forming *zig-zag* chains. The structure belongs to the family of linear intergrowth structures formed by AlB$_2$- and CaF$_2$-type slabs, in this case present in the ratio 1:2.

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Структурний тип ZrAl₀,₂₃Ge₁,₇₇

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Знайдено нову тернарну сполуку ZrAl₀,₂₃Ge₁,₇₇ при 600°C і її кристалічну структуру визначено методом рентгенівської дифракції монокристалу. Структура (власний тип, символ Пірсона *tI*32-8, просторова група *I*4₁/*amd*, *a* = 3,8013(2), *c* = 29,893(3) Å, *Z* = 4) є варіантом з частковим позиційним невпорядкуванням атомів псевдо-бінарного структурного типу Zr₀,₇₅AlSi₁,₂₅. Обидві структури належать до серії лінійних неоднорідних структур, побудованих зрощенням фрагментів типу AlB₂ (шари центрованих тригональних призм) і фрагментів типу CaF₂ (шари незаповнених "напів-октаедрів") у співвідношенні 1:2. Структура сполуки ZrAl₀,₂₃Ge₁,₇₇ характеризується статистичним розташуванням атомів Al і Ge в одному з кристалографічних положень, що утворюють фрагменти типу CaF₂, а також позиційним невпорядкуванням атомів Ge, які утворюють зигзагоподібні ланцюжки вздовж кристалографічного напрямку [100].

Ключові слова: цирконій; алюміній; германій; рентгенівська дифракція монокристалу; тернарна сполука; кристалічна структура; структура зрощення.