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Structural defects of rare-earth disilicides and digermanides

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Based on literature data and own experimental data the crystal structures of (defect) binary disilicides and digermanides of rare-earth metals (*R*) have been reviewed and discussed. In each of the binary systems *R*–{Si,Ge} up to six compounds of variable composition RSi_{2-x} or RGe_{2-x} (x = 0-0.5) are known. At certain compositions ordering of vacancies with formation of superstructures is observed. The electronic factor has a significant impact on the formation of a particular type of structure and it is shown that an essential criterion for the formation of stoichiometric and off-stoichiometric disilicides (digermanides) of rare-earth metals is the valence electron concentration per *p*-element atom (VEC_A), which should not exceed 8.3. The required value of VEC_A may be achieved by Si(Ge) vacancies, heterovalent substitution by Al or Ga atoms, or intergrowth with other structural segments.

Rare-earth metal / Silicide / Germanide / Crystal structure / Vacancy derivative / Structure series / Valence electron concentration

Introduction

For all the binary systems *R*–{Si,Ge}, where *R* is a rare-earth metal, with the exception of the {Eu,Tm,Lu}–Si systems, phase diagrams have been constructed, and for most of the compounds formed in these systems, the crystal structures are known [1-3]. However, more detailed studies are needed for disilicides and digermanides, where from 3 to 11 structure types have been reported [4,5]. In the *R*–Si systems, where *R* is a light rare-earth element, a full row of RSi_2 compounds with tetragonal α-$ThSi_2$-type structures is observed at high temperatures, while the orthorhombic α-$GdSi_2$-type is adopted at lower temperatures (exception Eu) (Table 1). At high temperatures the heavy rare-earth elements form a full row of isotypic compounds of composition $RSi_{1.67}$ with the hexagonal structure type AlB_2 [6]. In the *R*–Ge systems, the early rare-earth metals also form a full row (exception Eu) of compounds with the structure type α-$ThSi_2$ at high temperatures [7], but not at the stoichiometry 1:2. The structures of the low-temperature modifications belong to orthorhombic derivatives of the α-$ThSi_2$ type (Table 2). Similarly to the *R*–Si systems, in the *R*–Ge systems, representatives of the late rare-earth metals form compounds that crystallize with structures of the AlB_2 type, or closely related types in the case of Tm and Yb.

Consequently, the most common structure types among rare-earth disilicides and digermanides are AlB_2 (10 silicides and 8 germanides), α-$ThSi_2$ (8 and 8), and α-$GdSi_2$ (9 and 4). Structures of the AlB_2 and α-$ThSi_2$ types and their defective derivatives form in the concentration range 36.4-40.0 at.% *R*, *i.e.* the composition of the compounds differs from the ideal RSi_2 or RGe_2 stoichiometries and can be described by the formulas RSi_{2-x} or RGe_{2-x}, where x = 0.25-0.50, or R_4Ge_7, R_3Si_5 (R_3Ge_5), R_2Ge_3 when x = 1/4, 1/3, 1/2, respectively, and show partial Si or Ge defects. Defective derivatives of the hexagonal structure type AlB_2 with an ordered arrangement of vacancies that have been reported for rare-earth silicides and germanides are the hexagonal structure type Th_3Pd_5 [8] (16.7% vacancies) and the monoclinic structure type Tm_2Ge_3 [9] (25%) (Fig. 1). The representatives of the orthorhombic structure types $ErSi_{1.67}$ [10] (16.7%) and Er_3Si_{5-x} [11] (20.7%) exhibit partly ordered vacancies. Lowering of the temperature often promotes the ordering of vacancies. Defective derivatives of the tetragonal structure type α-$ThSi_2$ with ordered arrangements of vacancies are the orthorhombic types Nd_4Ge_7 [12] (12.5% vacancies) and Y_3Ge_5 [13] (16.7%) (Fig. 2), as well as the types $Gd_{17}Ge_{29}$ [13] (14.7%), $Ho_{14}Ge_{23}$ [13] (17.9%), $Dy_{11}Ge_{18}$ [13] (18.2%), and Ce_9Ge_{14} [14] (22.3%) with large unit cells. For off-stoichiometric compositions the orthorhombic structure type α-$GdSi_2$ [15] exhibits partial ordering of vacancies.

The aim of the present work was to study the reasons for structural defects in rare-earth disilicides and digermanides.

Table 1 Structure type, type and temperature (in K) of formation (*L* – from the melt, *P* – peritectic, *PD* – peritectoid, *T* – polymorphic transformation) of binary compounds RSi_{2-x}.

x	Structure type	La	Ce	Pr	Nd	Sm	Eu	Gd
~ 0 [1]	α-$ThSi_2$	$LaSi_2$ (*P*, ~1875)	$CeSi_2$ (*L*, 1893)	$PrSi_2$ (*L*, 1985)	$NdSi_2$ (*L*, 2030)	$SmSi_2$ (*L*, 2113)	$EuSi_2$ (...)	$GdSi_2$ (*L*, 2373)
~ 0.3	α-$GdSi_2$	$LaSi_{1.67}$ (*L*, 2003)	$CeSi_{1.67}$ (*P*, 1833)	$PrSi_2$ (*T*, 430)	$NdSi_2$ (*T*, 420)	$SmSi_2$ (*T*, 653)		$GdSi_2$ (*T*, 673)
~ 0.5	...				$NdSi_{1.5}$ (*PD*, 1780)			$GdSi_{1.5}$ (*PD*, 2073)
	AlB_2				$NdSi_{1.5}$ (*T*, 800)	$SmSi_{1.67}$ (*PD*, 1853)		$GdSi_{1.5}$ (*T*, 1393)

x	Structure type	Tb	Dy	Ho	Er	Tm	Yb	Lu
~ 0.2	α-$ThSi_2$		$DySi_{1.75}$ (*P*, 1703)					
	α-$GdSi_2$	$TbSi_2$ (*P*, 1790)	$DySi_{1.75}$ (*T*, 813)	$HoSi_{1.82}$ (*P*, 793)				
~ 0.3	AlB_2	$TbSi_{1.67}$ (*P*, 1911)	$DySi_{1.6}$ (*P*, 1908)	$HoSi_{1.67}$ (*P*, 1893)	$ErSi_{1.67}$ (*P*, 1893)	$TmSi_{1.67}$ (...)	$YbSi_{1.8}$ (*P*, 1698)	$LuSi_{1.67}$ (...)
	...		$DySi_{1.6}$ (*T*, 1033)	$HoSi_{1.67}$ (*T*, 1073)	$ErSi_{1.67}$ (*T*, 1078)			
	$ErSi_{1.67}$				$ErSi_{1.67}$ (?, 15)			
	Th_3Pd_5						Yb_3Si_5 (*PD*, 1238)	

[1] compositions near 1:2 need to be confirmed

Relationship between structural defects and valence electron concentration

Based on literature data and own experimental investigations carried out in several systems [16] it was found that the main criterion for the formation of rare-earth silicides and germanides with the structure types AlB_2, α-$ThSi_2$ and vacancy derivatives of these is the valence electron concentration. For a (hypothetical) compound $R^{3+}Si_2$ or $R^{3+}Ge_2$ (Si and Ge are located on the Zintl line), the number of valence electrons per *p*-element atom (A = anion), by analogy with ionocovalent compounds [17], can be calculated by the formula:

$$VEC_A = [(1\times 3\bar{e}(R) + 2\times 4\bar{e}(A)) / 2] + AA = 5.5 + AA.$$

After having received 3 electrons from each rare-earth atom, to fill the outer electron shell (octet), each Si or Ge atom still needs 2.5 additional electrons, which it may receive by forming *n* homoatomic A–A bonds (AA). In the defect-free structures of the AlB_2 and α-$ThSi_2$ types, the Si or Ge atoms form flat nets or frameworks, where each atom participates in three homoatomic bonds. It follows from the formula above that $VEC_A = 8.5$, *i.e.* part of the valence electrons are not localized in bonds.

In fact, for the compounds with structure types AlB_2, α-$ThSi_2$ and derivatives considered here, the number of Si–Si or Ge–Ge bonds per *p*-element atom is slightly less than three, due to partial vacancies. For the deficient structures of RSi_{2-x} or RGe_{2-x}, the average number of A–A bonds per Si or Ge atom (AA) can be calculated by the formula:

$$AA = \frac{6(1-x)}{2-x}.$$

The valence electron concentration per anion will be equal to:

$$VEC_A = 4 + \frac{3}{2-x} + \frac{6(1-x)}{2-x} = \frac{17-10x}{2-x}.$$

In Table 3 VEC_A values for particular compositions are given. As can be seen, at the composition $R^{3+}Si_{1.5}$ or $R^{3+}Ge_{1.5}$ (R_2Ge_3) the compound can be assimilated to a polyanionic valence compound [17].

In the systems *R*–Si and *R*–Ge the structure types AlB_2, α-$ThSi_2$ and derivatives are formed at a valence electron concentration per Si or Ge atom of VEC_A = 8-8.3. This value does not correspond to the ideal stoichiometry 1:2, but is achieved thanks to vacancies on the Si or Ge sites. For the compounds considered here there is a clear tendency toward higher numbers of vacancies in the structure type AlB_2, compared to the structure type α-$ThSi_2$, which may be due to the configuration of the anion sublattices (two-dimensional nets in the former, a three-dimensional framework in the latter). VEC_A values smaller than 8 are unlikely.

Replacement of part of the Si or Ge atoms with four valence electrons by Al or Ga atoms with three valence electrons will lead to a decrease of the VEC_A values. However, this heterovalent substitution is usually accompanied by the inclusion of additional small atoms, which in turn increases the value of VEC_A. For solid solutions based on binary compounds and truly ternary compounds $R\mathrm{Si}_{2\text{-}x\text{-}y}\mathrm{Al}_y\square_x$ with the structure types AlB_2, α-$ThSi_2$ and derivatives, the valence electron concentration per anion can be represented by the formula:

$$VEC_A = C + \frac{3}{2-x} + \frac{6(1-x)}{2-x} = C + \frac{3(3-2x)}{2-x},$$

$$C = \frac{[\mathrm{Al(Ga)}]\times 3 + [\mathrm{Si(Ge)}]\times 4}{[\mathrm{Al(Ga)}] + [\mathrm{Si(Ge)}]},$$

where [Al(Ga)] and [Si(Ge)] are the number of atoms of the corresponding elements in one formula unit.

Table 2 Structure type, type and temperature (K) of formation (*L* – from the melt, *P* – peritectic, *PD* – peritectoid, *T* – polymorphic) of binary compounds $R\mathrm{Ge}_{2\text{-}x}$.

x	Structure type	La	Ce	Pr	Nd	Sm	Eu	Gd
~ 0	$EuGe_2$						$EuGe_2$ (...)	
~ 0.1	$TbGe_2$ ($PrGe_{1.91}$)			$PrGe_{1.91}$ (...)				$GdGe_{1.97}$ (...)
~ 0.3	α-$ThSi_2$	$LaGe_{1.6}$ (*L*, 1500)	$CeGe_{1.67}$ (*L*, 1513)	$PrGe_{1.6}$ (*L*, 1506)	$NdGe_{1.6}$ (*L*, 1487)	$SmGe_2$ (*PD*, 760)		$GdGe_{1.63}$ (*PD*, 808)
	Nd_4Ge_7	La_4Ge_7 (...)	Ce_4Ge_7 (...)	Pr_4Ge_7 (...)	Nd_4Ge_7 (...)	Sm_4Ge_7 (...)		
	Y_3Ge_5	La_3Ge_5 (...)	Ce_3Ge_5 (*T*, 560)	Pr_3Ge_5 (*T*, 615)	Nd_3Ge_5 (...)	Sm_3Ge_5 (...)		Gd_3Ge_5 (*T*, 600)
	α-$GdSi_2$	$LaGe_{1.6}$ (*T*, 455)	$CeGe_{1.75}$ (...)	$PrGe_2$ (*PD*, 615)	$NdGe_{1.6}$ (*T*, 680)			
	$YGe_{1.7}$			$PrGe_{1.6}$ (...)				
~ 0.5	AlB_2					$SmGe_{1.5}$ (*P*, 1355)		$GdGe_{1.56}$ (*T*, 833)

x	Structure type	Tb	Dy	Ho	Er	Tm	Yb	Lu
~ 0	$ErGe_{2.16}$				$ErGe_{2.16}$ (...)			
	$ZrSi_2$					$Tm_{0.9}Ge_2$ (*P*, 1158)		$LuGe_{1.8}$ (*P*, 1338)
~ 0.1	$TbGe_2$ ($PrGe_{1.91}$)	$TbGe_2$ (*P*, 1213)	$DyGe_{1.90}$ (...)					
	$TmGe_{1.9}$					$TmGe_{1.9}$ (*P*, 1295)		
~ 0.2	$DyGe_{1.85}$		$DyGe_{1.85}$ (*P*, 1240)		$ErGe_{1.83}$ (*T*, 1180)	$TmGe_{1.83}$ (*P*, 1313)		
	$YGe_{1.82}$			$HoGe_{1.85}$ (*P*, 1273)				
~ 0.3	α-$ThSi_2$	Tb_3Ge_5 (*P*, 1653)		Ho_3Ge_5 (*P*, 1513)				
	Y_3Ge_5	Tb_3Ge_5 (*T*, 1163)	Dy_3Ge_5 (*P*, 1208)	Ho_3Ge_5 (*T*, 1213)				
	Th_3Pd_5						Yb_3Ge_5 (*P*, 1348)	
~ 0.5	AlB_2	$TbGe_{1.5}$ (*P*, 1693)	$DyGe_{1.5}$ (*P*, 1676)	$HoGe_{1.5}$ (*P*, 1673)	$ErGe_{1.5}$ (*P*, 1678)		$YbGe_{1.5}$ (*L*, 1353)	$LuGe_{1.5}$ (*P*, 1603)
	Tm_2Ge_3					Tm_2Ge_3 (*P*, 1545)		

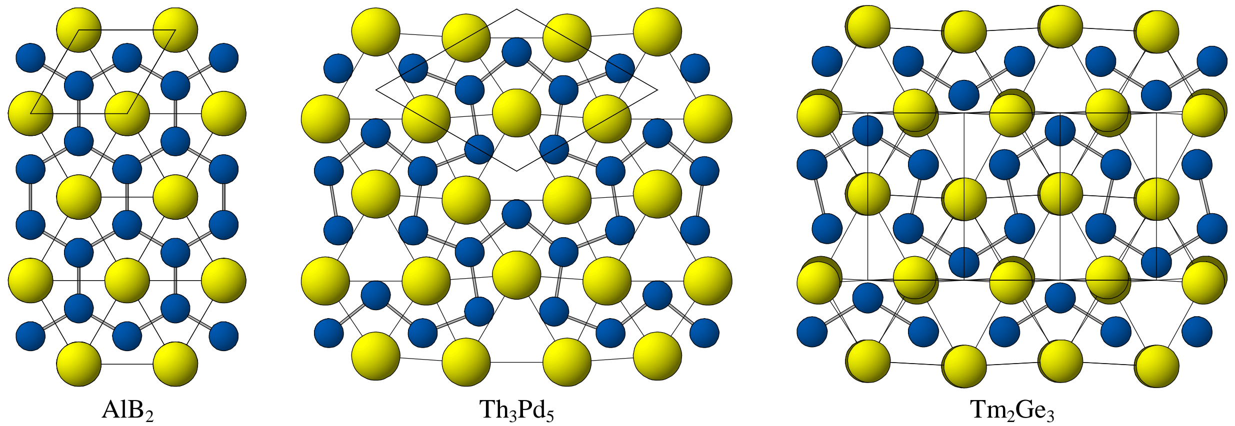

Fig. 1 Structure type AlB_2 and ordered vacancy derivatives.

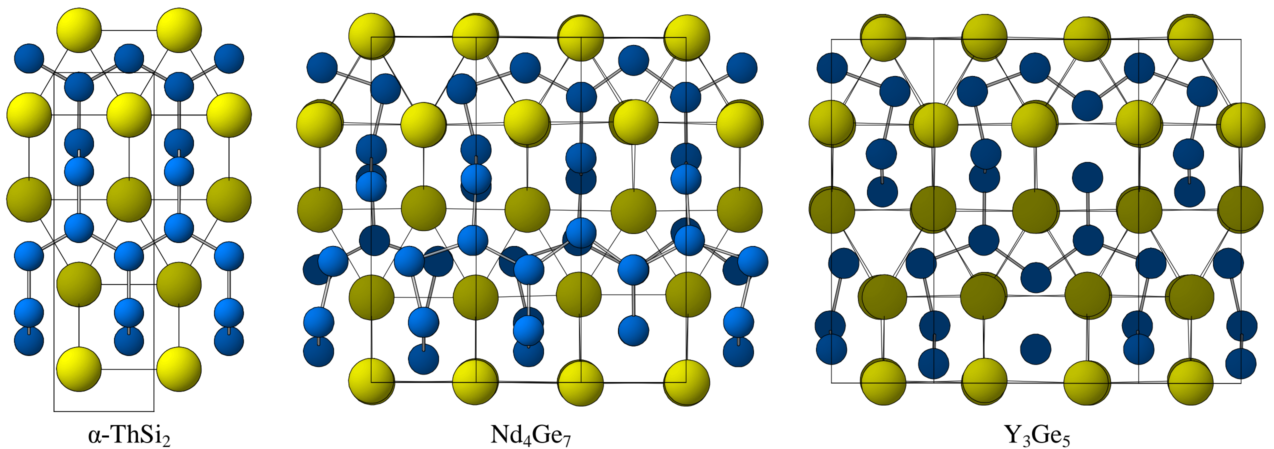

Fig. 2 Structure type α-$ThSi_2$ and ordered vacancy derivatives.

Table 3 Valence electron concentration per anion for $R\text{Si}_{2-x}$, $R\text{Ge}_{2-x}$, and $R(\text{Ge,Si})_{2-x}$ compounds with the structure types AlB_2, α-$ThSi_2$ and derivatives (AA = average number of anion-anion bonds per anion, VEC_A = valence electron concentration per anion).

Composition	*R*, at.%	*x*	AA	VEC_A
$R^{3+}\text{Si}_{1.5}$ $R^{3+}\text{Ge}_{1.5}$ ($R_2\text{Ge}_3$)	40.0	0.50	2	8
$\text{Er}^{3+}\text{Ge}_{0.82}\text{Si}_{0.70}$	39.7	0.48	2.05	8.03
$\text{Er}^{3+}\text{Si}_{1.59}$ ($\text{Er}_3\text{Si}_{4.76}$)	38.9	0.41	2.09	8.11
$R^{3+}\text{Si}_{1.67}$ ($R_3\text{Si}_5$) $R^{3+}\text{Ge}_{1.67}$ ($R_3\text{Ge}_5$)	37.5	0.33	2.40	8.19
$\text{Er}^{3+}\text{Ge}_{1.00\text{-}0.73}\text{Si}_{0.67\text{-}0.94}$	37.5	0.33	2.40	8.19
$R^{3+}\text{Si}_{1.75}$ $R^{3+}\text{Ge}_{1.75}$ ($R_4\text{Ge}_7$)	36.4	0.25	2.57	8.29
$R^{3+}\text{Si}_2$ [1] $R^{3+}\text{Ge}_2$ [1]	33.3	0	3	8.50
$\text{Eu}^{2+}\text{Si}_2$ $\text{Eu}^{2+}\text{Ge}_2$ [2]	33.3	0	3	8

[1] compounds reported with these compositions need to be confirmed; [2] own structure type (space group *P*-3*m*1) [18], which is a deformation derivative of the AlB_2 type

Table 4 Valence electron concentration per anion for ternary compounds and solid solutions $R(Al,Si)_{2-x}$, $R(Al,Ge)_{2-x}$, and $R(Ga,Ge)_{2-x}$ with the structure types AlB_2, α-$ThSi_2$ and derivatives in the systems {Gd,Er}–{Al,Ga}–(Si,Ge} (C = average number of valence electrons provided by each anion counting 3 for Al(Ga) and 4 for Si(Ge), AA = average number of anion-anion bonds per anion, VEC_A = valence electron concentration per anion).

Composition	R, at.%	x	C	AA	VEC_A
$Gd^{3+}Al_{0.23}Si_{1.33}$ [1]	39.1	0.44	3.85	2.15	7.93
$Gd^{3+}Al_{0.26}Ge_{1.28}$ [1]	39.4	0.46	3.88	2.10	7.93
$Er^{3+}Ga_{0.41\text{-}0.58}Si_{1.21\text{-}1.11}$	38.2-37.2	0.38-0.31	3.75-3.66	2.30-2.45	7.90-7.88
$Er^{3+}Ga_{0.13}Si_{1.57}$ [1]	37.1	0.30	3.92	2.47	8.16
$Er^{3+}Al_{0.14}Ge_{1.57}$ [1]	36.9	0.29	3.92	2.49	8.17
$Gd^{3+}Al_{0.42}Ge_{1.36}$ [1]	36.0	0.22	3.76	2.63	8.07
$Gd^{3+}Al_{0.89}Si_{0.89}$	36.0	0.22	3.50	2.63	7.81
$Gd^{3+}AlGe$	33.3	0	3.50	3	8
$Er^{3+}Ga_{1.48}Si_{0.52}$	33.3	0	3.26	3	7.76

[1] limiting composition of the substitutional / interstitial solid solution

In Table 4 the results of calculations for several rare-earth silicides and germanides containing aluminum or gallium are presented. The value of VEC_A is in the range 7.8-8.2, and at the equiatomic composition the compound GdAlGe (structure type α-$ThSi_2$) exhibits the characteristics of a polyanionic valence compound.

Linear structure series with AlB_2-type (α-$ThSi_2$) segments

In the binary R–Ge and ternary R–{Al,Ga}–Ge systems the compounds RGe_{2-x}, $R(Al,Ge)_{2-x}$, and $R(Ga,Ge)_{2-x}$ with $x < 0.25$ crystallize in the structure types $ErGe_{2.16}$ [19], $ZrSi_2$ [20], $TbGe_2$ [21], $PrGe_{1.91}$ [22], $TmGe_{1.9}$ [23], $DyGe_{1.85}$ [24], and $YGe_{1.82}$ [25] (Table 5). These types belong to a linear inhomogeneous series of structures based on segments of the simple types hexagonal AlB_2 (space group *P*6/*mmm*) and cubic CaF_2 (*Fm*-3*m*) [26]. The AlB_2-type segments are layers of trigonal prisms R_6 centered by the smaller atoms, which have common bases and also share two of the three rectangular faces with neighboring prisms. The CaF_2-type segments are double layers of empty tetragonal antiprisms formed by four R atoms and four small atoms, the two layers having common atoms (small) and being related by a mirror or a glide plane [5].

In the orthorhombic structure types $TbGe_2$ and $PrGe_{1.91}$, blocks of three layers of trigonal prisms (arrangement of adjacent layers as in the type α-$ThSi_2$) are separated by a double layer characteristic of the type CaF_2 (Fig. 3). The $PrGe_{1.91}$ (*Cmmm*) type differs from the $TbGe_2$ (*Cmmm*) type by a shift of most of the Ge atoms from their ideal positions, and the existence of disordered Ge vacancies in the central layer of the three-layer block of trigonal prisms.

The orthorhombic structure types $DyGe_{1.85}$ (*Cmc*2$_1$) and $YGe_{1.82}$ (*Cmcm*) contain the same ratio (3:1) of AlB_2- and CaF_2-type segments as the structures discussed above. However, the layers of trigonal prisms in these structures are fused as in the AlB_2 type (all prism axes parallel). The two structure types differ in the displacements of the Ge atoms that center the prisms in the middle layer of the three-layer blocks of trigonal prisms.

The ratio of AlB_2- and CaF_2-type segments in the orthorhombic structures of the $ErGe_{2.16}$ and $ZrSi_2$ types is 1:1. The $ErGe_{2.16}$ (*Cmcm*) type is an example of insertion of additional small atoms into the CaF_2-type segments (tetragonal antiprisms) of the $ZrSi_2$ (*Cmcm*) type. In the closely related type $ZrGa_2$ (*Cmmm*), two fused CaF_2-type layers are related by a mirror plane. In the $TmGe_{1.9}$ (*Pmma*) type, three-layer blocks of trigonal prisms and single layers of prisms alternate, separated by CaF_2-type segments.

A linear inhomogeneous structure series based on segments of the simple types hexagonal AlB_2 and cubic W (*Im*-3*m*) [27] (Fig. 3) is also known. The W-type segments are layers of empty R_4 tetrahedra that have common faces and edges [5]. In this series, the analogue of the structure type $YGe_{1.82}$ is the orthorhombic type V_2B_3 (*Cmcm*) [28], where the ratio of AlB_2- and W-type segments is 3:1 and the AlB_2-type layers contain prisms fused as in AlB_2. It should be noted that this structure type is adopted by Si-deficient silicides R_2Si_{3-x}, where R is Ce, Pr, Nd, Tb, Ho, x = 0-0.5. The ternary orthorhombic types $Pr_4Al_3Ge_3$ (*Cmcm*) [29] and $Er_4Ga_{2.72}Si_{3.28}$ (*C*2*cm*) [30] are analogues of the binary type $TbGe_2$ (binary analogues are not known). The two structures are similar, but in $Er_4Ga_{2.72}Si_{3.28}$ two of the five atom sites are split and the distribution of p-element atoms is different [30]. The structure of another ternary aluminum germanide, $Ba_3Al_2Ge_2$ (*Immm*, superstructure of the type Ta_3B_4) [31], adopted by $Eu_3Al_{1.8}Ge_2$ [32], where Eu probably contributes two rather than three electrons, can be obtained by merging two AlB_2-type segments and one W-type segment.

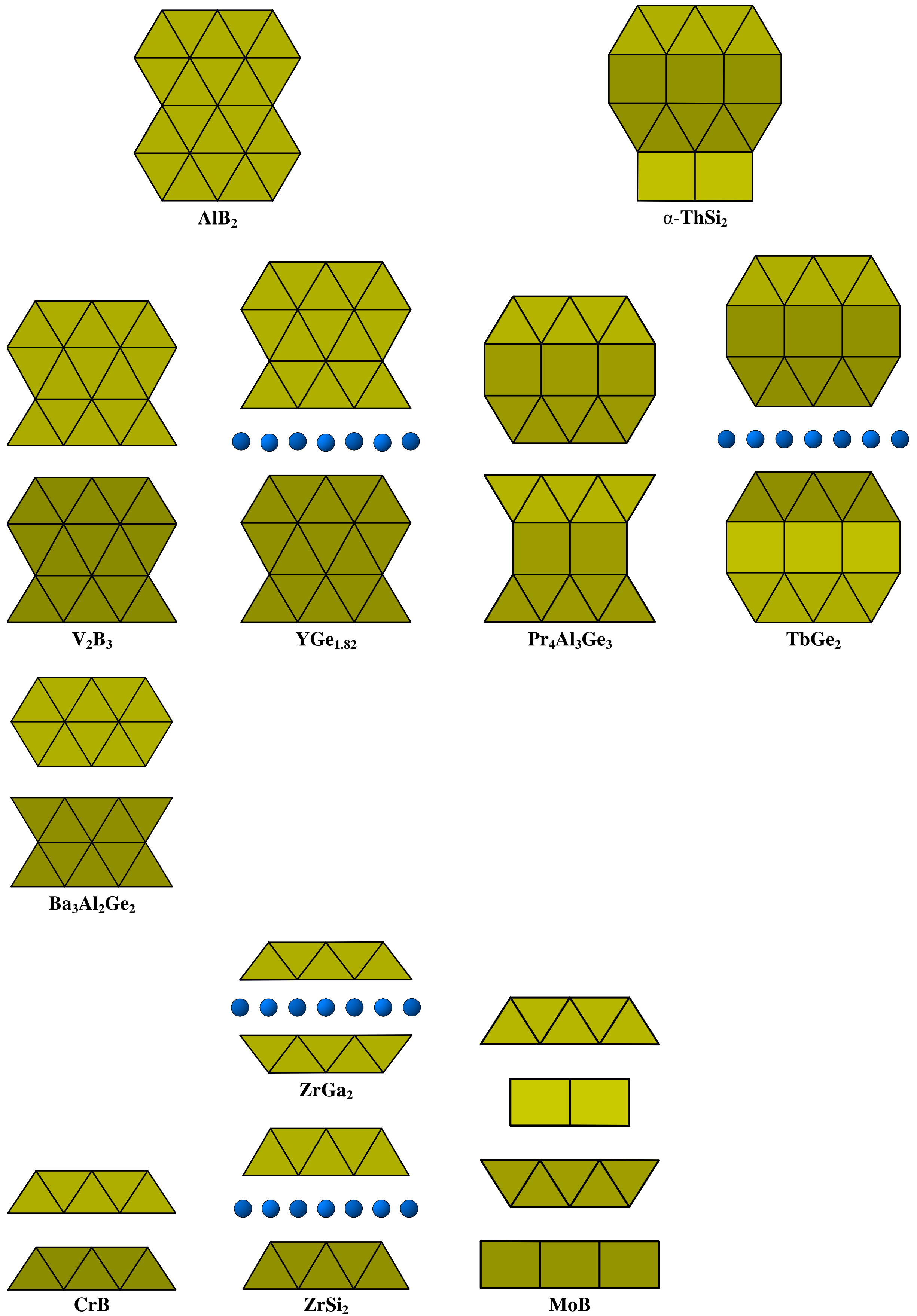

Fig. 3 Structure types belonging to the linear inhomogeneous structure series with AlB_2- and W- or CaF_2-type segments.

Table 5 Formation (filled fields) of compounds RGe_{2-x}, $R(Al,Ge)_{2-x}$, and $R(Ga,Ge)_{2-x}$ with intergrowth structures containing AlB_2- and CaF_2-type segments.

Structure type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
R–Ge systems														
$ErGe_{2.16}$ / $ZrSi_2$											■	■		■
$TbGe_2$ / $PrGe_{1.91}$			■				■	■	■					
$DyGe_{1.85}$ / $YGe_{1.82}$									■	■	■	■		
R–Al–Ge systems														
$ErGe_{2.16}$ / $ZrSi_2$							■	■	■	■	■			
$TbGe_2$ / $PrGe_{1.91}$	■	■	■	■	■									
R–Ga–Ge systems														
$ErGe_{2.16}$ / $ZrSi_2$											■			
$TbGe_2$ / $PrGe_{1.91}$										■				

An analogue of the structure type $ZrSi_2$ is the orthorhombic type TlI (*Cmcm*), often referred to as CrB for intermetallics [33]. Structures of this type are observed for rare-earth monosilicides and monogermanides. In the structure of the tetragonal type MoB ($I4_1/amd$) [34], as in CrB the ratio of AlB_2- and W-type segments is 1:1, but subsequent layers of trigonal prisms are rotated by 90°.

Valence electron concentration for intergrowth structures

Despite the lower number of vacancies in the compounds RGe_2, $R(Al,Ge)_2$, and $R(Ga,Ge)_2$ ($x < 0.25$) with intergrowth structures built from AlB_2- (α-$ThSi_2$) and CaF_2-type segments, in comparison with binary and ternary compounds with structures of the AlB_2, α-$ThSi_2$ types or derivatives ($x = 0.25$-0.50), the valence electron concentration VEC_A does not exceed 8.3 for the binary and 8.2 for the ternary compounds (see Table 6). For compounds with structures of the types $TbGe_2$ ($PrGe_{1.91}$) and $YGe_{1.82}$ ($DyGe_{1.85}$) the average number of A–A bonds per Ge atom can be calculated by the formula:

$$AA = \frac{22-17x}{x^2-6x+8}.$$

Based on experimental data, we assume that defects occur at atom sites that center three-capped trigonal prisms (three homoatomic bonds for full occupation), and that the Ge atoms in the CaF_2-type segments form three homoatomic bonds, which represents the average value for the two boundary cases – a square net and a zigzag chain. The number of valence electrons per anion for a binary rare-earth germanide RGe_{2-x} is equal to:

$$VEC_A = 4 + \frac{6}{4-x} + \frac{22-17x}{x^2-6x+8},$$

which becomes, in the case of a ternary compound with aluminum (gallium):

$$VEC_A = C + \frac{6}{4-x} + \frac{22-17x}{x^2-6x+8},$$

$$C = \frac{[Al(Ga)]\times 3 + [Ge]\times 4}{[Al(Ga)] + [Ge]},$$

where [Al(Ga)] and [Ge] is the number of Al(Ga) and Ge atoms, respectively, in the formula unit.

Table 6 Number of valence electrons per anion for $RGe_{2\pm x}$, $R(Al,Ge)_{2-x}$, and $R(Ga,Ge)_{2-x}$ compounds with intergrowth structures containing AlB_2- (α-$ThSi_2$) and CaF_2-type segments (C = average number of valence electrons provided by an anion, AA = average number of anion-anion bonds per anion, VEC_A = valence electron concentration per anion).

Composition	Structure type	*R*, at.%	*x*	C	AA	VEC_A
$Er^{3+}Ge_{2.16}$	$ErGe_{2.16}$	31.6	0.16	4	2.91	8.30
$Gd^{3+}Al_{0.15}Ge_{2.01}$	$ErGe_{2.16}$	31.6	0.16	3.93	2.91	8.23
$Er^{3+}Al_{0.15}Ge_{1.92}$	$ErGe_{2.16}$	32.5	0.07	3.93	2.69	8.07
$Er^{3+}Al_{0.15}Ge_{1.85}$ $Er^{3+}Ga_{0.15}Ge_{1.85}$	$ZrSi_2$	33.3	0	3.93	2.50	7.93
$Ho^{3+}Ga_{0.15}Ge_{1.85}$	$PrGe_{1.91}$				2.75	8.18
$Tb^{3+}Ge_2$	$TbGe_2$	33.3	0	4	2.75	8.25
$Pr^{3+}Ge_{1.91}$	$PrGe_{1.91}$	34.4	0.09	4	2.74	8.27
$Gd^{3+}Ge_{1.97}$	$PrGe_{1.91}$	33.7	0.03	4	2.75	8.26
$Dy^{3+}Ge_{1.85}$	$DyGe_{1.85}$	35.1	0.15	4	2.73	8.29
$Y^{3+}Ge_{1.82}$	$YGe_{1.82}$	35.5	0.18	4	2.72	8.29

For a stoichiometric binary rare-earth germanide of the structure type $ZrSi_2$ ($R^{3+}Ge_2$) AA = (3 + 2) / 2 = 2.5, and VEC_A = 4 + 3/2 + 2.5 = 8. Larger values of VEC_A are reached by inserting additional germanium atoms into voids of the structure, *e.g.* adopting the type $ErGe_{2.16}$. The calculations were performed according to the following formulas:

$$\mathrm{AA} = \frac{5+8x}{2+x},$$

$$\mathrm{VEC_A} = \mathrm{C} + \frac{3}{2+x} + \frac{5+8x}{2+x} = \mathrm{C} + \frac{8(1+x)}{2+x}.$$

The empirical limiting valence electron concentration per *p*-element atom, VEC_A is 8.3 (binary compounds) and $VEC_A \leq 8.2$ (ternary compounds), is also observed for silicides with the structure type V_2B_3 ($VEC_A = 8.18$ for the composition $R_2Si_{2.5}$) and the ternary compounds $Pr_4Al_3Ge_3$ (8.17) and $Er_4Ga_{2.72}Si_{3.28}$ (8.21). The limiting value of $VEC_A \approx 8.3$ is observed for $R^{3+}Ge_{1.75}$ compounds ($x = 0.25$) with structure types AlB_2, α-$ThSi_2$ or derivatives, $Y^{3+}Ge_{1.82}$ ($x = 0.18$), $Pr^{3+}Ge_{1.91}$ ($x = 0.09$), and $Er^{3+}Ge_{2.16}$ ($x = -0.16$).

Conclusions

It is shown that the valence electron concentration is an essential criterion for the formation of rare-earth germanides (silicides) with the structure types AlB_2, α-$ThSi_2$, or vacancy derivatives of these. The same observation was made for representatives of the series of structures based on AlB_2- and CaF_2- or W-type slabs. For all these compounds, the maximum valence electron concentration per *p*-element atom (VEC_A) is 8.3. The required value of VEC_A is achieved by vacancies on the sites occupied by Si(Ge) atoms, different arrangements of structural segments, or heterovalent substitution of part of the Si or Ge atoms by Al or Ga atoms. For the ternary compounds, the highest empirical value observed for VEC_A is 8.2.

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References

[1] T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, American Society for Metals, Materials Park, OH, USA, 1986, Vols. 1-4, 2224 p.

[2] H. Okamoto (Ed.), *Desk Handbook: Phase Diagrams for Binary Alloys*, American Society for Metals, Materials Park, OH, USA, 2000, 828 p.

[3] P. Villars, K. Cenzual, J.L.C. Daams, F. Hulliger, H. Okamoto, K. Osaki, A. Prince, S. Iwata (Eds.), *Pauling File, Inorganic Materials Database and Design System, Binaries Edition*, Crystal Impact (Distributor), Bonn, Germany, Release 2002/1.

[4] E.I. Gladyshevskii, *Crystal Chemistry of Silicides and Germanides*, Metallurgy, Moscow, 1971, 296 p. (in Ukrainian).

[5] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *TYPIX. Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*, Springer-Verlag, Berlin, Germany, 1993/1994, Vols. 1-4, 1596 p.

[6] E.J. Felten, *J. Am. Chem. Soc.* 78 (1956) 5977-5978.

[7] G. Brauer, A. Mitius, *Z. Anorg. Allg. Chem.* 249 (1942) 325-339.

[8] J.R. Thomson, *Acta Crystallogr.* 16 (1963) 320-321.

[9] G. Venturini, I. Ijjaali, B. Malaman, *J. Alloys Compd.* 284 (1999) 262-269.

[10] V. Ghetta, E. Hoossay, A. Rouault, R. Madar, B. Lambert, *C. R. Acad. Sci., Ser. II* 309 (1989) 995-1000.

[11] S. Pukas, L. Akselrud, R. Cerny, R. Gladyshevskii, *Chem. Met. Alloys* 1 (2008) 185-191 (in Ukrainian).

[12] G. Venturini, I. Ijjaali, B. Malaman, *J. Alloys Compd.* 289 (1999) 168-177.

[13] G. Venturini, I. Ijjaali, B. Malaman, *J. Alloys Compd.* 285 (1999) 194-203.

[14] B. Lambert, E. Houssay, R. Madar, F. Hippert, J. Pierre, S.Auffret, *J. Less-Common Met.* 167 (1990) 53-63.

[15] J.A. Perri, I. Binder, B. Post, *J. Phys. Chem.* 63 (1959) 616-619.

[16] S. Pukas, *Thesis*, Ivan Franko National University of Lviv, 2008.

[17] E. Parthé, *Elements of Inorganic Structural Chemistry*, K. Sutter Publisher, Petit-Lancy, Switzerland, 1990, 158 p.; *Елементи неорганічної структурної хімії*, Світ, Lviv, 1993, 104 p. (in Ukrainian).

[18] E.I. Gladyshevskii, *Zh. Strukt. Khim.* 5 (1964) 568-575 (in Russian).

[19] G. Venturini, I. Ijjaali, B. Malaman, *J. Alloys Compd.* 288 (1999) 183-187.

[20] S.V. Naray Szabo, *Z. Kristallogr.* 97 (1937) 223-228.

[21] P. Schobinger Papamantellos, D.B. De Mooij, K.H.J. Buschow, *J. Less-Common Met.* 144 (1988) 265-274.

[22] I. Savysyuk, N. Semuso, R. Gladyshevskii, *Chem. Met. Alloys* 10 (2017) 45-97.

[23] G. Venturini, *J. Alloys Compd.* 308 (2000) 200-204.

[24] I.R. Mokra, V.K. Pecharskii, Z.M. Shpyrka, O.I. Bodak, V.K. Belskii, I.E. Patz, *Dopov. Akad. Nauk Ukr. RSR, Ser. B* 3 (1989) 45-47 (in Ukrainian).

[25] I. Ijjaali, G. Venturini, B. Malaman, *J. Alloys Compd.* 284 (1999) 237-242.
[26] W.L. Bragg, *Proc. R. Soc. London, Ser. A* 89 (1914) 468-489.
[27] P. Debye, *Phys. Z.* 18 (1917) 483-488.
[28] Y. Yu, L.E. Tergenius, T. Lundström, S. Okada, *J. Alloys Compd.* 221 (1995) 86-90.
[29] E.I. Gladyshevskii, N.Z. Semuso, R.E. Gladyshevskii, K. Cenzual, J.L. Jorda, *Chem. Met. Alloys* 1 (2008) 352-359.
[30] S.Ya. Pukas, R. Cerny, M.B. Manyako, R.E. Gladyshevskii, *Ukr. Khim. Zh.* 73(11) (2007) 18-26 (in Ukrainian).
[31] A. Widera, B. Eisenmann, H. Schäfer, K. Turban, *Z. Naturforsch. B* 31 (1976) 1592-1595.
[32] B. Bauer, C. Röhr, *Z. Naturforsch. B* 66 (2011) 793-812.
[33] F. Bertaut, P. Blum, *Acta Crystallogr.* 4 (1951) 66-67.
[34] R. Kiessling, *Acta Chem. Scand.* 1 (1947) 893-916.