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Crystal structures of the compounds $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3

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Two gadolinium alumogermanides, $GdAl_{0.09(3)}Ge_{2.07(4)}$ and Gd_2AlGe_3, were synthesized by arc melting and their crystal structures were studied by X-ray powder diffraction. The compound $GdAl_{0.09}Ge_{2.07}$ crystallizes with an $ErGe_{2.16}$-type structure: Pearson symbol *oS*16, space group *Cmcm*, *a* = 4.1704(5), *b* = 16.447(2), *c* = 3.9820(5) Å. It is the second known representative of the structure type $ErGe_{2.16}$ (a binary variant of the type $CeNiSi_2$) among rare-earth alumogermanides; in both cases Al was found to partially substitute for Ge on one of the fully occupied Ge sites. The compound Gd_2AlGe_3 is isostructural to Y_2AlGe_3: Pearson symbol *oP*24, space group *Pnma*, *a* = 6.8031(2), *b* = 4.2282(1), *c* = 17.8165(5) Å, and is the ninth representative of this type. Common to the two structures is the presence of layers of Ge-centered Gd_6 trigonal prisms sharing the bases and two of the three lateral faces.

Gadolinium / Aluminum / Germanium / X-ray powder diffraction / Crystal structure

Introduction

The interaction of the components in the Gd–Al–Ge system at 500°C has been investigated in the concentration range 0-33.3 at.% Gd [1]. The existence of two previously known compounds, $GdAl_2Ge_2$ (structure type Ce_2SO_2 [2]) and GdAlGe (α-$ThSi_2$ [3]), was confirmed, the formation of a new ternary intermetallide of approximate composition $GdAlGe_2$ with unknown structure was established, and the isothermal cross-section of the phase diagram was constructed. Six more compounds were later reported in the same system: Gd_2AlGe_6 (La_2AlGe_6) [4], $Gd_2Al_3Ge_4$ ($Ba_2Cd_3Bi_4$) [5], $Gd_2Al_{3.05}Ge_3$ ($Tb_2Al_{3.15}Ge_3$) [6], $GdAl_{0.35}Ge_2$ ($CeNiSi_2$) [7], Gd_2AlGe_2 (Ca_2Ir_2Si) [8], and $Gd_{11}Al_2Ge_8$ ($Sc_{11}Al_2Ge_8$) [9]. The compound ~$GdAlGe_2$ probably corresponds to the compound $Gd_2Al_{1.4}Ge_{5.6}$.

The compound GdAlGe exists in two modifications: the crystal structure of the room-temperature modification adopts the orthorhombic structure type YAlGe [10], whereas the crystal structure of the high-temperature modification belongs to the tetragonal α-$ThSi_2$ structure type [3] (investigation at 500°C), or its ordered ternary derivative LaPtSi [10] (600°C). According to [11], at 1000°C the compound with equiatomic composition is part of the homogeneity range $GdAl_xGe_{2-x}$ (x = 0-1), *i.e.* of the solid solution of Al in the binary compound $GdGe_2$. Hence, in total, eight ternary compounds have been reported in the Gd–Al–Ge system [12] (Table 1).

In this work the results of a structural investigation of two new ternary gadolinium alumogermanides, $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3, are presented.

Experimental

Samples of nominal compositions $Gd_{30}Al_5Ge_{65}$ and $Gd_{33.3}Al_{16.7}Ge_{50}$ were synthesized from high-purity metals (Gd ≥ 99.86 wt.%, Al ≥ 99.998 wt.%, and Ge ≥ 99.999 wt.%) by arc-melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components, the samples were melted twice. The ingots were annealed at 800°C under vacuum in quartz ampoules for 1 month and subsequently quenched in cold water. The weight losses during the preparation of the samples were less than 1 % of the total mass, which was 1 g for each alloy.

The phase and structural analyses were performed based on X-ray powder diffraction data collected on a diffractometer HZG-4a (Cu *K*α radiation, angular range 20 ≤ 2θ ≤ 110°, step 0.05°, scan time 20 s, sample $Gd_{30}Al_5Ge_{65}$) or STOE STADI P (Cu $K\alpha_1$ radiation, angular range 6 ≤ 2θ ≤ 100.005°, step 0.015°, scan time 250 s, sample $Gd_{33.3}Al_{16.7}Ge_{50}$). The structures were refined by the Rietveld method, using the program DBWS-9807 [13]. The structure drawings were made with the program ATOMS [14].

Table 1 Crystallographic parameters of compounds reported in the Gd–Al–Ge system.

Compound	Structure type	Pearson symbol	Space group	*a*, Å	*b*, Å	*c*, Å	Ref.
$GdAl_2Ge_2$	Ce_2SO_2	*hP*5	*P*-3*m*1	4.184	–	6.662	[2]
Gd_2AlGe_6	La_2AlGe_6	*mS*36	*C*2/*m*	8.041	8.351 β = 100.81°	10.546	[4]
$Gd_2Al_3Ge_4$	$Ba_2Cd_3Bi_4$	*oS*36	*Cmce*	5.948	14.875	7.762	[5]
$Gd_2Al_{3.05}Ge_3$	$Tb_2Al_{3.15}Ge_3$	*hR*234	*R*-3*c*	7.2764	–	8.8587	[6]
$GdAl_{0.35}Ge_2$	$CeNiSi_2$	*oS*16	*Cmcm*	4.0874	16.1499	3.9372	[7]
GdAlGe rt	YAlGe	*oS*12	*Cmcm*	4.010	10.314	5.704	[10]
GdAlGe ht	α-$ThSi_2$	*tI*12	$I4_1/amd$	4.152	–	14.42	[3]
	LaPtSi	*tI*12	$I4_1md$	4.1521	–	14.415	[10]
Gd_2AlGe_2	Ca_2Ir_2Si	*mS*20	*C*2/*c*	10.126	5.6837 β = 104.729°	7.7683	[8]
$Gd_{11}Al_2Ge_8$	$Sc_{11}Al_2Ge_8$	*tI*84	*I*4/*mmm*	10.9924	–	16.3026	[9]

Results and discussion

The alloys used for the structural analysis, $Gd_{30}Al_5Ge_{65}$ and $Gd_{33.3}Al_{16.7}Ge_{50}$, were single-phase samples and contained the phases $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3, respectively. Experimental details and crystallographic data for both compounds are presented in Table 2. Atomic coordinates, isotropic displacement parameters and occupancies for $GdAl_{0.09}Ge_{2.07}$ are given in Table 3, atomic coordinates and isotropic displacement parameters for Gd_2AlGe_3 in Table 4. The isotropic displacement parameters of atoms of the same chemical element were constrained to be equal.

Particular features of the refined structure of the compound $GdAl_{0.09}Ge_{2.07}$ ($ErGe_{2.16}$-type structure, Pearson symbol *oS*16, space group *Cmcm* [15]) are the statistical mixture of Ge and Al atoms on one of the three sites occupied by small atoms, and the partial occupancy of another one by Ge atoms (16 %). A similar distribution of the atoms was reported for $ErAl_{0.15}Ge_{1.92}$ [16]. The structure of $GdAl_{0.09}Ge_{2.07}$ is isopointal to the structure of the compound $GdAl_{0.35}Ge_2$. In the latter ($CeNiSi_2$ type, *oS*16, *Cmcm*) two of the three sites of small atoms are fully occupied by Ge atoms and one site is partly occupied by Al atoms (35 %) [7]. In the case of $GdAl_{0.35}Ge_2$, the sample was annealed at 600°C and we do not exclude the existence of a certain homogeneity range (including the compositions $GdAl_{0.09}Ge_{2.07} \equiv Gd_{32}Al_3Ge_{65}$ and $GdAl_{0.35}Ge_2 \equiv Gd_{30}Al_{10}Ge_{60}$), within which a slight redistribution of the atoms takes place. A reinvestigation of this apparently quite complex part of the phase diagram would be useful. However, differently from the isotypic compound in the Er–Al–Ge system, the Gd-containing compound is truly ternary, because a binary gadolinium germanide with $ErGe_{2.16}$-type structure does not exist.

The structure of the compound Gd_2AlGe_3 (Y_2AlGe_3, *oP*24, *Pnma* [17]) shows ordered distribution of the atoms: the Gd atoms occupy two sites, the Al atoms one and the Ge atoms three sites, all of them being fully occupied. Observed and calculated diffraction diagrams for the samples $Gd_{30}Al_5Ge_{65}$ and $Gd_{33.3}Al_{16.7}Ge_{50}$ are shown in Figs. 1 and 2. Interatomic distances and conventional coordination polyhedra in $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3 are given in Tables 5 and 6, respectively.

In the structure of $GdAl_{0.09}Ge_{2.07}$ (see Table 5) the coordination polyhedron of the Gd atoms has 15 vertices and can be described as a hexagonal prism of composition $Ge_{10}M_2$ with three additional atoms: two of these correspond to the statistical mixture of Al and Ge atoms and the third one belongs to the site Ge2, which is partly occupied. The Ge atoms from the site Ge1 are situated inside Gd_6 trigonal prisms, the rectangular faces of which are capped by Ge atoms from both sites (Ge1 and Ge2). The coordination polyhedron of the Ge atoms from the site Ge2 has 10 vertices and can be described as two square pyramids of compositions Gd_5 and GeM_4, which are oriented in opposite ways and interpenetrate. The Al and Ge atoms from the statistical mixture (site *M*) are situated inside a 12-vertex polyhedron, which can be decomposed into two tetrahedra of compositions Gd_4 and Ge_4 and one square of composition M_4.

As can be seen from Table 6, in the structure of Gd_2AlGe_3 the Gd atoms center slightly deformed square and pentagonal prisms consisting of two Al and six or eight Ge atoms, with one (Al) or two (Al and Ge), respectively, additional atoms located above lateral faces. The coordination polyhedron of the Al atoms has 12 vertices and can be decomposed into a tetragonal pyramid of composition Gd_5, a tetrahedron of composition Ge_4 and three additional atoms (two Al and one Ge). Two of the three sites of Ge atoms (Ge1 and Ge2) are characterized by trigonal-prismatic coordination (prism composition Gd_6). The prisms are capped by one Al and two Ge atoms, located above the rectangular faces. In the case of the site Ge3, the coordination polyhedron has the shape of a strongly deformed trigonal prism of composition Gd_4Al_2 with one additional Al atom above a rectangular face.

Comparing the structures of the compounds $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3, one notes the similar environment of the Ge atoms, which are in both cases located inside straight trigonal prisms built up exclusively of Gd atoms. Layers of trigonal prisms (infinite in two directions, common triangular and rectangular faces) can be seen (Fig. 3). In the case of $GdAl_{0.09}Ge_{2.07}$ the layers of trigonal prisms alternate with two heavily deficient layers of Ge atoms (partly occupied site Ge2) and one layer of Al and Ge atoms (site *M*), and in the case of Gd_2AlGe_3 with two layers of Al and two layers of Ge atoms.

The compound Gd_2AlGe_3 is the ninth representative of the Y_2AlGe_3 structure type identified up to now. The cell parameters of the isotypic compounds R_2AlGe_3, listed in Table 7, decrease with decreasing radius of the trivalent rare-earth metal [20] from Sm to Tm. In the compound Yb_2AlGe_3, Yb shows the valency 2+ [19].

Table 2 Details of the refinements of the structures of $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3.

Compound		$GdAl_{0.09(3)}Ge_{2.07(4)}$	Gd_2AlGe_3
Structure type		$ErGe_{2.16}$	Y_2AlGe_3
Space group		*Cmcm*	*Pnma*
Cell parameters:	*a*, Å	4.1704(5)	6.8031(2)
	b, Å	16.447(2)	4.2282(1)
	c, Å	3.9820(5)	17.8165(5)
Cell volume *V*, $Å^3$		273.12(6)	512.49(2)
Formula units per cell *Z*		4	4
Diffractometer		HZG-4a	STOE STADI P
Radiation type, wavelength λ, Å		Cu *K*α, 1.5418	Cu $K\alpha_1$, 1.5406
Density D_X, g cm^{-3}		7.536	7.246
Scale factor		$0.235(3)\cdot 10^{-4}$	$0.595(3)\cdot 10^{-4}$
FWHM parameters *U*, *V*, *W*		0.45(8), -0.25(7), 0.08(1)	0.117(7), -0.032(5), 0.015(1)
Mixing parameter η		0.60(3)	0.639(9)
Asymmetry parameter C_M		-0.04(3)	-0.084(7)
Texture parameter *G* [direction]		0.985(6) [010]	1.009(2) [001]
Number of reflections		130	402
Number of refined parameters		19	26
Reliability factors R_B, R_p, R_{wp}		0.0944, 0.0150, 0.0194	0.0932, 0.0132, 0.0172
Goodness of fit *S*		0.38	0.62

Table 3 Atom coordinates and isotropic displacement parameters for $GdAl_{0.09}Ge_{2.07}$: structure type $ErGe_{2.16}$, *oS*16, *Cmcm*, *a* = 4.1704(5), *b* = 16.447(2), *c* = 3.9820(5) Å.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, $Å^2$	Occ.
Gd	4*c*	0	0.3959(6)	¼	0.71(5)	1
Ge1	4*c*	0	0.0480(7)	¼	0.73(9)	1
Ge2	4*c*	0	0.178(3)	¼		0.16(1)
M^a	4*c*	0	0.7508(8)	¼		1

[a] $M = Al_{0.09(3)}Ge_{0.91(3)}$.

Table 4 Atom coordinates and isotropic displacement parameters for Gd_2AlGe_3: structure type Y_2AlGe_3, *oP*24, *Pnma*, *a* = 6.8031(2), *b* = 4.2282(1), *c* = 17.8165(5) Å.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, $Å^2$
Gd1	4*c*	0.1676(4)	¼	0.4154(2)	0.83(5)
Gd2	4*c*	0.1713(4)	¼	0.2032(2)	
Ge1	4*c*	0.0268(6)	¼	0.6757(3)	1.12(7)
Ge2	4*c*	0.1461(6)	¼	0.8136(3)	
Ge3	4*c*	0.2453(6)	¼	0.0358(2)	
Al	4*c*	0.4549(19)	¼	0.5648(8)	1.8(3)

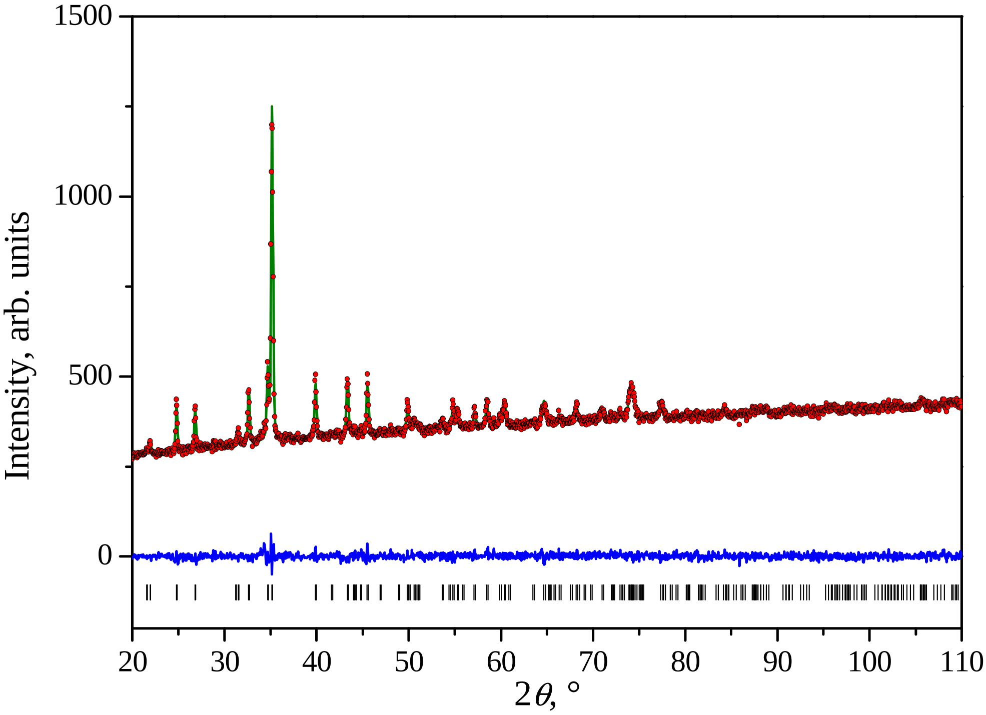


Fig. 1 Observed (dots), calculated (line) and difference (bottom) X-ray powder diffraction patterns (Cu *K*α radiation) for the sample $Gd_{30}Al_5Ge_{65}$ (vertical bars indicate peak positions of $GdAl_{0.09}Ge_{2.07}$).

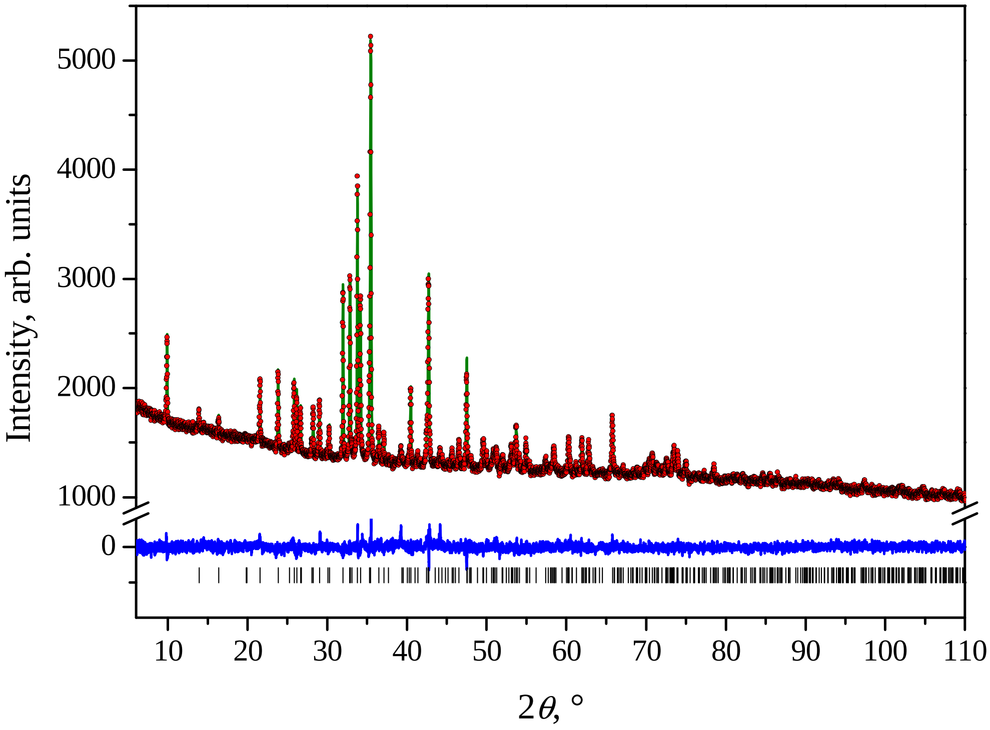
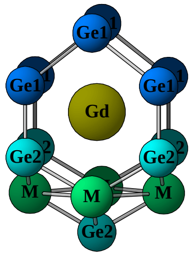
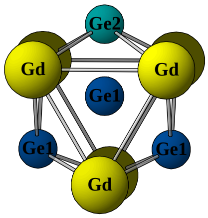
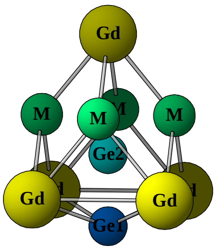
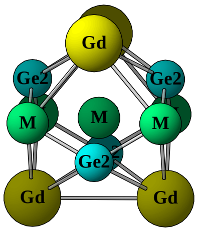


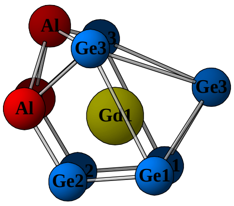
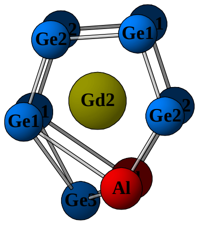
Fig. 2 Observed (dots), calculated (line) and difference (bottom) X-ray powder diffraction patterns (Cu $K\alpha_1$ radiation) for the sample $Gd_{33.3}Al_{16.7}Ge_{50}$ (vertical bars indicate peak positions of Gd_2AlGe_3).

Table 5 Interatomic distances and coordination polyhedra (assuming full occupancy of site Ge2) for $GdAl_{0.09}Ge_{2.07}$.

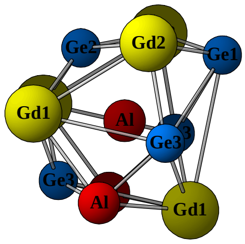
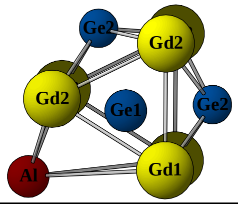
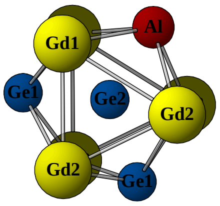
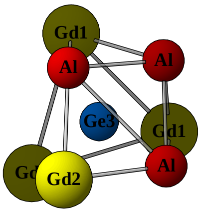
Atoms		δ, Å	Polyhedron
Gd	-4 Ge1	3.027(5)	
	-2 M[a]	3.128(13)	
	-4 Ge2[b]	3.129(18)	
	-2 M[a]	3.169(12)	
	-2 Ge1	3.257(12)	
	-1 Ge2[b]	3.58(5)	
Ge1	-1 Ge2[b]	2.14(5)	
	-2 Ge1	2.541(10)	
	-4 Gd1	3.027(5)	
	-2 Gd1	3.257(12)	
Ge2[b]	-1 Ge1	2.14(5)	
	-2 M[a]	2.309(26)	
	-2 M[a]	2.405(25)	
	-4 Gd	3.129(18)	
	-1 Gd	3.58(5)	
M[a]	-2 Ge2[b]	2.309(26)	
	-2 Ge2[b]	2.405(25)	
	-4 M[a]	2.8832(3)	
	-2 Gd	3.128(13)	
	-2 Gd	3.169(12)	

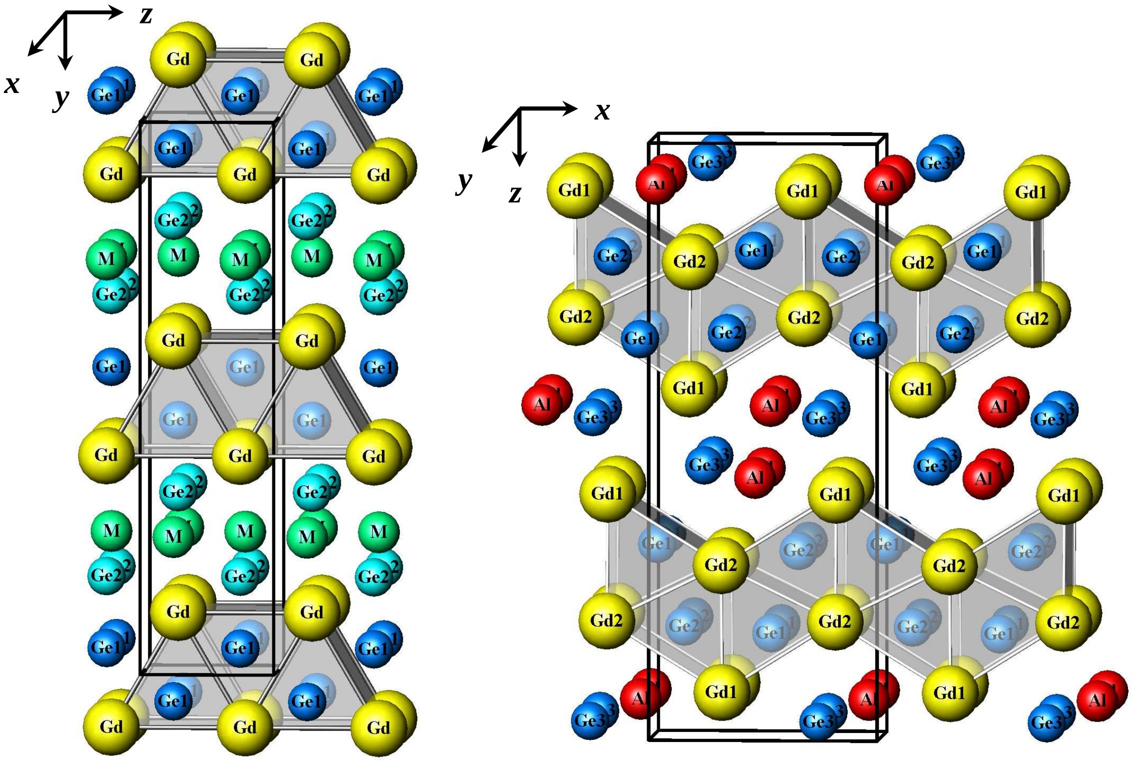
[a] $M = Al_{0.09(3)}Ge_{0.91(3)}$,
[b] partly occupied site, occ. = 0.16(1).

Table 6 Interatomic distances and coordination polyhedra for Gd_2AlGe_3.

Atoms		δ, Å	Polyhedron
Gd1	-2 Ge1	2.975(4)	
	-1 Ge3	3.002(5)	
	-2 Ge2	3.060(4)	
	-2 Ge3	3.069(4)	
	-1 Al	3.302(14)	
	-2 Al	3.345(10)	
Gd2	-2 Ge1	2.988(4)	
	-1 Ge3	3.025(5)	
	-2 Ge2	3.037(4)	
	-2 Ge2	3.144(5)	
	-2 Ge1	3.308(5)	
	-2 Al	3.359(11)	

Continuation of **Table 6**

Atoms		δ, Å	Polyhedron
Al	-1 Ge2	2.527(15)	
	-2 Ge3	2.567(8)	
	-1 Ge3	2.668(14)	
	-2 Al	3.190(15)	
	-1 Gd1	3.302(14)	
	-2 Gd1	3.345(10)	
	-2 Gd2	3.359(11)	
	-1 Ge1	3.519(14)	
Ge1	-2 Ge2	2.588(7)	
	-2 Gd1	2.975(4)	
	-2 Gd2	2.988(4)	
	-2 Gd2	3.308(5)	
	-1 Al	3.519(14)	
Ge2	-1 Al	2.527(15)	
	-1 Ge1	2.588(7)	
	-1 Ge1	2.597(6)	
	-2 Gd2	3.037(4)	
	-2 Gd1	3.060(4)	
	-2 Gd2	3.144(5)	
Ge3	-2 Al	2.567(8)	
	-1 Al	2.668(14)	
	-1 Gd1	3.002(5)	
	-1 Gd2	3.025(5)	
	-2 Gd1	3.069(4)	



$GdAl_{0.09}Ge_{2.07}$ ($ErGe_{2.16}$, *Cmcm*) Gd_2AlGe_3 (Y_2AlGe_3, *Pnma*)

Fig. 3 The structures of the gadolinium alumogermanides $GdAl_{0.09}Ge_{2.07}$ and Gd_2AlGe_3; the Gd_6 trigonal prisms centered by Ge atoms are emphasized.

Table 7 Cell parameters of R_2AlGe_3 compounds with Y_2AlGe_3-type structures.

Compound	r_R, Å	a, Å	b, Å	c, Å	V, Å^3	Ref.
Sm_2AlGe_3	1.802	6.8153	4.2723	17.9491	522.62	[18]
Gd_2AlGe_3	1.802	6.8031(2)	4.2282(1)	17.8165(5)	512.49(2)	this work
Y_2AlGe_3 ^{a}	1.801	6.785	4.189	17.676	502.39	[17]
Tb_2AlGe_3	1.782	6.7749	4.1980	17.7222	504.04	[18]
Dy_2AlGe_3	1.773	6.785	4.171	17.665	499.92	[17]
Ho_2AlGe_3	1.766	6.753	4.158	17.580	493.63	[17]
Er_2AlGe_3	1.757	6.746	4.1401	17.535	489.74	[16]
Tm_2AlGe_3	1.746	6.706	4.061	17.550	477.94	[17]
Yb_2AlGe_3 ^{a}	1.940 ^{b}	6.8220	4.1787	18.139	517.09	[19]

^{a} single-crystal data,
^{b} for Yb^{2+}.

Conclusions

The structure of the ternary compound $GdAl_{0.09}Ge_{2.07}$ belongs to the $ErGe_{2.16}$ type (Pearson symbol *oS*16, space group *Cmcm*). A particular feature of the $ErGe_{2.16}$ type is the partial occupancy (16 %) of one of the three Ge sites (Ge2). In the case of the compound $GdAl_{0.09}Ge_{2.07}$, this site is also occupied by Ge atoms, whereas the Al atoms form a statistic mixture with Ge atoms on one of two fully occupied sites (*M*). In the structure of the ternary compound Gd_2AlGe_3 (structure type Y_2AlGe_3, Pearson symbol *oP*24, space group *Pnma*) ordered distribution of the atoms is observed.

One of the three sites occupied by small atoms in the structure of the compound $GdAl_{0.09}Ge_{2.07}$ (Ge1), and two of the four sites of small atoms in the structure of the compound Gd_2AlGe_3 (Ge1 and Ge2), are characterized by trigonal-prismatic coordination (prism composition Gd_6). These prisms form infinite layers by sharing the triangular and two of the rectangular faces.

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