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$MgAl_2Ge_2$ – a new representative of the structure type $CaAl_2Si_2$

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The magnesium alumogermanide $MgAl_2Ge_2$ was synthesized in a high-frequency furnace and its crystal structure was studied by X-ray powder diffraction. It crystallizes with a $CaAl_2Si_2$-type structure: Pearson symbol *hP*5, space group *P*-3*m*1, *a* = 4.11693(5), *c* = 6.7873(1) Å. For the isotypic compounds RAl_2M_2 (*R* = Mg, Ca, Sr, *M* = Si, Ge) on increasing the ratio of the covalent radii r_M/r_R (from 0.700 for $SrAl_2Si_2$ to 0.982 for $MgAl_2Ge_2$) the *R*-centered elongated trigonal antiprisms M_6 become compressed, whereas the initially compressed trigonal pyramids M_4 centered by Al become elongated. The trigonal structure type $CaAl_2Si_2$ can be derived from the hexagonal structure type AlB_2 *via* the structure types ZrBeSi and γ-EuPtP.

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

1. Introduction

More than 400 ternary compounds have been reported to crystallize with a structure that belongs to the prototype Ce_2SO_2 [1], or its “antitype” $CaAl_2Si_2$ [2] (Si_2CaAl_2) [3,4]. The latter structure type is commonly used in the case of intermetallic compounds. In the structure type $CaAl_2Si_2$ (space group *P*-3*m*1) the Ca atoms occupy the one-fold Wyckoff position 1*a* (0 0 0) and correspond to the S atoms in the structure of Ce_2SO_2. The Al and Si atoms orderly occupy two two-fold sites in Wyckoff position 2*d* (⅓ ⅔ *z*) and correspond to the O and Ce atoms, respectively, in the prototype.

The compounds from the above mentioned family are representatives of different chemical classes: chalcogenides (oxides, sulfides, selenides, and tellurides), pnictides (nitrides, phosphides, arsenides, antimonides, and bismutides), and compounds containing an element of group IV of the periodic system (carbides, silicides, and germanides). It should be noted, that all known isotypic compounds with C, Si, or Ge (34) contain aluminum and half of them (17) are germanides. As can be seen from Table 1, alumogermanides form with alkaline-earth (Ca and Sr) and rare-earth (Y and La-Lu) metals. Alumosilicides (16) also form with alkaline-earth (Mg, Ca, and Sr) and rare-earth (Y, La-Er, and Yb) metals and there is also one alumocarbide with Mg. The absence of compounds $MgAl_2Ge_2$, $TmAl_2Si_2$, and $LuAl_2Si_2$ is unexpected.

The aim of the present work was to search for a new representative of the structure type $CaAl_2Si_2$ in the system Mg–Al–Ge and determine its structural parameters.

2. Experimental

12 three-component alloys were synthesized from the elements (purity of Mg ≥ 99.4 wt.%, Al ≥ 99.998 wt.%, and Ge ≥ 99.999 wt.%) in sealed niobium tubes in a high-frequency furnace. The weight loss during the preparation of the samples was less than 1% of the total mass, which was 0.4 g.

Phase analysis was performed based on X-ray powder diffraction data collected on a DRON-2.0M diffractometer (Fe *K*α radiation, λ = 1.9374 Å), using the program POWDER CELL [5] and the database TYPIX [6].

The crystal structure of the new compound was refined on X-ray powder diffraction data. The intensity data for the polycrystalline sample $Mg_{20}Al_{40}Ge_{40}$ were collected on an automatic diffractometer STOE STADI P (Cu $K\alpha_1$ radiation, λ = 1.5406 Å, in the angular range $6 \leq 2\theta \leq 120.24°$ with scan step 0.015° and scan time 250 s). The structural parameters were refined by the Rietveld method, using the program DBWS-9807 [7]. Projections of the structures were drawn by the program ATOMS [8].

Table 1 Ternary compounds with $CaAl_2Si_2$-type structure in the systems *R*–Al–*M* (*R* = Mg, Ca, Sr, Y, La-Lu, *M* = C, Si, Ge) [3,4].

Compound	Mg	Ca	Sr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RAl_2C_2	+																	
RAl_2Si_2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	
RAl_2Ge_2	(+)[a]	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

[a] This work.

Table 2 Details of the structural refinement for $MgAl_2Ge_2$.

Space group	*P*-3*m*1
Cell parameters *a*, *c*, Å	4.11693(5), 6.7873(1)
Cell volume *V*, $Å^3$	99.627(3)
Formula units per cell *Z*	1
Density D_X, g cm^{-3}	3.723
FWHM parameters *U*, *V*, *W*	0.141(6), 0.049(5), 0.0019(9)
Mixing parameter η	0.711(4)
Asymmetry parameter C_M	0.030(3)
Texture parameter *G*	1.393(2) [001]
Number of reflections	86
Number of refined parameters	15
Reliability factors R_B, R_p, R_{wp}	0.0604, 0.0560, 0.0779
Goodness of fit *S*	1.04

Table 3 Atomic coordinates and isotropic displacement parameters for $MgAl_2Ge_2$.

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, $Å^2$
Mg	1*a*	0	0	0	0.88(2)
Al	2*d*	⅓	⅔	0.6353(3)	0.59(2)
Ge	2*d*	⅓	⅔	0.2419(2)	0.48(2)

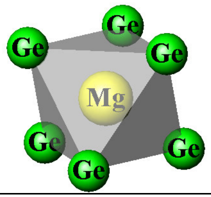
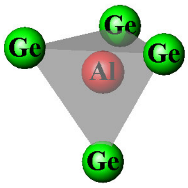
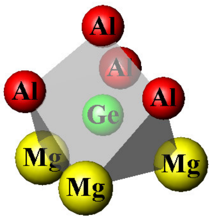
3. Results and discussion

The X-ray phase analysis of the alloys showed that all the synthesized samples, with the exception of $Mg_{20}Al_{40}Ge_{40}$, were multi-phase samples and contained as one of the phases Mg_2Ge with the cubic structure type CaF_2 (Pearson symbol *cF*12, space group *Fm*-3*m*, *a* = 6.3818(2) Å for the sample $Mg_{67}Al_{10}Ge_{23}$). According to the phase diagram of the binary system Mg–Ge [3] this compound is formed directly from the liquid at 1117°C. The formation of one more binary compound, $Mg_{17}Al_{12}$ with own cubic structure type (Pearson symbol *cI*58, space group *I*-43*m*, *a* = 10.5858(6) Å for the sample $Mg_{50}Al_{40}Ge_{10}$), was confirmed. The alloy of nominal composition $Mg_{20}Al_{40}Ge_{40}$ appeared to be single-phase and contained the phase $MgAl_2Ge_2$, which was not known so far. This phase was also present in several other alloys. Based on X-ray diffraction data of the alloy $Mg_{20}Al_{40}Ge_{40}$ the structural parameters were determined and it was confirmed that the crystal structure of the new compound belongs to the type $CaAl_2Si_2$.

Details of the structural refinement (pseudo-Voigt function for profile) of the compound $MgAl_2Ge_2$ are presented in Table 2. The smaller atoms (Al and Ge) occupy two sites in Wyckoff position 2*d* of the space group *P*-3*m*1 in an ordered manner, and the larger atoms (Mg) the Wyckoff position 1*a*. The atomic coordinates and displacement parameters are given in Table 3, and the interatomic distances and atom polyhedra are listed in Table 4. The atomic environment of Mg and Al consists only of Ge atoms: octahedra (composition Ge_6) and tetrahedra (composition Ge_4), respectively. The Ge atoms are situated inside octahedra built up by Mg and Al atoms (composition Mg_3Al_3) with one additional Al atom in front of the triangular face formed by Al atoms. The observed and calculated diffraction diagrams are shown in Fig. 1.

Unit-cell parameters for the isotypic compounds in the systems {Mg, Ca, Sr}–Al–{C, Si, Ge} are listed in Table 5; the smallest values are observed for the carbon-containing compound and the largest values for the compounds with germanium. In the rows of isotypic alumosilicides and alumogermanides the unit-cell parameters increase with increasing ionic radius of the alkaline-earth metal from Mg to Sr ($r_{Mg^{2+}}$ = 0.72 Å, $r_{Ca^{2+}}$ = 1.00 Å, $r_{Sr^{2+}}$ = 1.18 Å for coordination number 6 [13]) (Fig. 2).

Table 4 Interatomic distances and coordination polyhedra for $MgAl_2Ge_2$.

Atoms		δ, Å	Polyhedron
Mg	-6 Ge	2.8888(8)	
Al	-3 Ge -1 Ge	2.5188(8) 2.6701(24)	
Ge	-3 Al -1 Al -3 Mg	2.5188(8) 2.6701(24) 2.8888(8)	

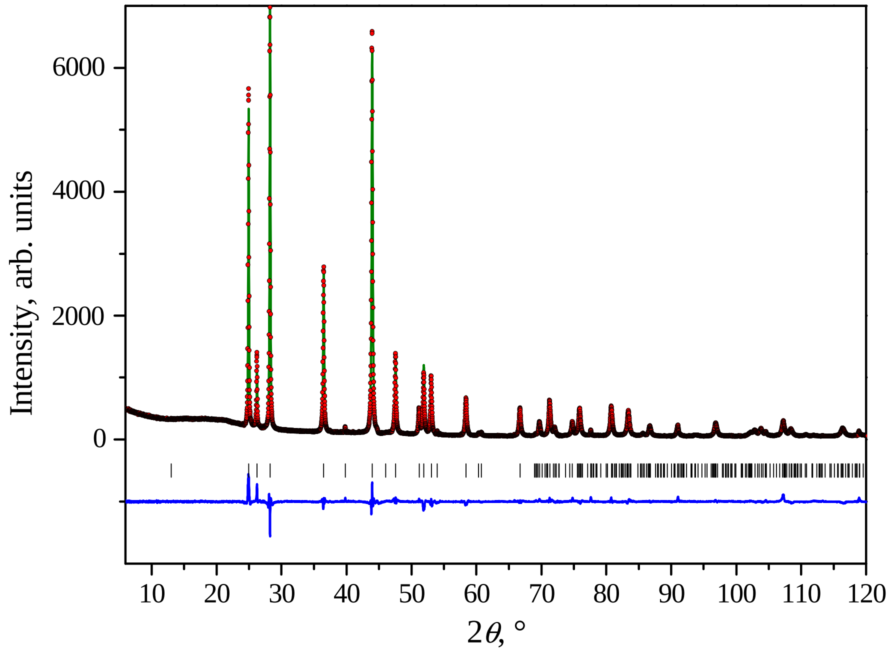


Fig. 1 Observed (dots), calculated (line) and difference (bottom) X-ray diffraction powder patterns (Cu $K\alpha_1$ radiation) for the sample $Mg_{20}Al_{40}Ge_{40}$ (vertical bars indicate peak positions of the compound $MgAl_2Ge_2$).

Interatomic distances within the coordination polyhedra for the above mentioned compounds are compared in Table 6 (for $SrAl_2Ge_2$ the atomic coordinates were not refined). The distances between the Al and Si atoms in the Al-centered Si_4 tetrahedra are in the range 2.489-2.520 Å (for the three Si atoms in a plane perpendicular to the 3-fold axis) and 2.572-2.62 Å (for the fourth Si atom, located on the 3-fold axis). The corresponding distances between Al and Ge atoms for Al-centered Ge_4 tetrahedra are 2.5188-2.533 and 2.639-2.6701 Å. These distances are in agreement with the sums of the covalent radii of the elements: r_{Al} = 1.230 Å (tetrahedral coordination), r_{Si} = 1.239 Å, r_{Ge} = 1.343 Å (octahedral coordination) [14].

Table 5 Cell parameters of compounds with $CaAl_2Si_2$-type structure in the systems {Mg, Ca, Sr}–Al–{C, Si, Ge}; ideal values are 0.8165 for c/a and 0.25 for z_M.

Compound	a, Å	c, Å	V, Å^3	c/a	Deviation from ideal c/a, %	z_M	Deviation from ideal z_M, %	Reference
$MgAl_2C_2$	3.377	5.817	57.5	1.723	+5.5	0.2654	+6.2	[9]
$MgAl_2Si_2$	4.05	6.74	95.7	1.664	+1.9	0.2463	-1.5	[10]
$MgAl_2Ge_2$	4.11693(5)	6.7873(1)	99.627(3)	1.649	+1.0	0.2419	-3.2	this work
$CaAl_2Si_2$	4.130	7.145	105.5	1.730	+5.9	0.27	+8.0	[2]
$CaAl_2Ge_2$	4.175	7.173	108.3	1.718	+5.2	0.2617	+4.7	[11]
$SrAl_2Si_2$	4.1834	7.4104	112.3	1.771	+8.5	0.2761	+10.4	[12]
$SrAl_2Ge_2$	4.225	7.448	115.1	1.763	+8.0	...	...	[2][a]

[a] Atomic coordinates not refined.

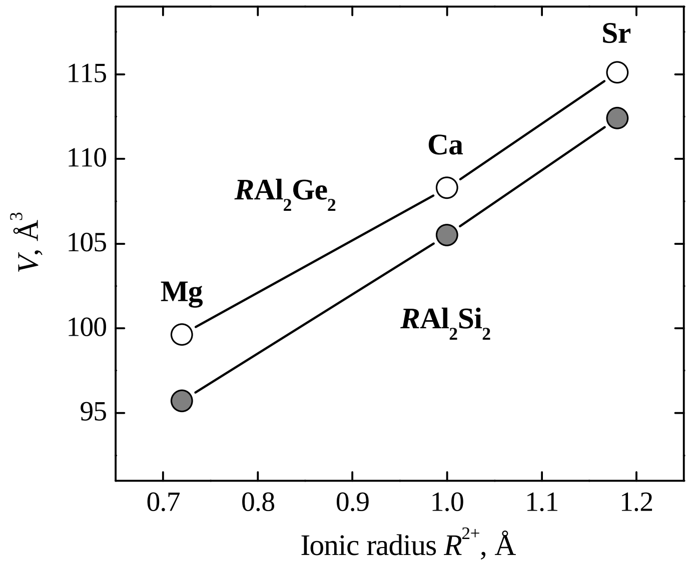


Fig. 2 Cell volume for RAl_2M_2 compounds *versus* the ionic radius of the alkaline-earth metal.

Table 6 Interatomic distances for the compounds RAl_2M_2 (R = Mg, Ca, Sr, M = C, Si, Ge).

Atoms		δ, Å						
		$MgAl_2C_2$ [9]	$MgAl_2Si_2$ [10]	$MgAl_2Ge_2$ this work	$CaAl_2Si_2$ [2]	$CaAl_2Ge_2$ [11]	$SrAl_2Si_2$ [12]	$SrAl_2Ge_2$ [2][a]
R	-6 M	2.487	2.85	2.8888(8)	3.067	3.055	3.165	...
Al	-3 M	2.055	2.49	2.5188(8)	2.489	2.533	2.520	...
	-1 M	2.078	2.62	2.6701(24)	2.572	2.639	2.598	...
M	-3 Al	2.055	2.49	2.5188(8)	2.489	2.533	2.520	...
	-1 Al	2.078	2.62	2.6701(24)	2.572	2.639	2.598	...
	-3 R	2.487	2.85	2.8888(8)	3.067	3.055	3.165	...

[a] Atomic coordinates not refined.

The Al-M and R-M distances do not give information about deformations of the Al-centered M_4 tetrahedra and the R-centered M_6 octahedra. Deformations of the octahedra towards trigonal antiprisms and of the tetrahedra towards trigonal pyramids are presented in Table 7. They were calculated as the difference between the observed and ideal ratios of the height of the coordination polyhedron to the edge length (Fig. 3). The heights (h) of the trigonal antiprism M_6 and trigonal pyramid M_4 were calculated along the 3-fold axes as $h = 2c\times z_M$ and $h = 2c\times(0.5-z_M)$, respectively. The edge length (l) corresponds to the unit-cell parameter a, and the ideal ratio $h/l = (⅔)^{½} = 0.8165$ for both kinds of polyhedron. Deformation with the sign "+" indicates elongation of the trigonal antiprism or pyramid along the 3-fold axis, whereas deformation with the sign "-" indicates compression. Deformation as a function of the ratio of

Table 7 Deformation of the M_6 octahedra (trigonal antiprisms) and M_4 tetrahedra (trigonal pyramids) around the R and Al atoms, respectively, for the compounds RAl_2M_2 (R = Mg, Ca, Sr, M = C, Si, Ge).

Compound	r_M/r_R [a]	Height of the trigonal antiprism (h), Å	Edge of the trigonal antiprism (l), Å	h/l	Deformation of the trigonal antiprism, %	Height of the trigonal pyramid (h), Å	Edge of the trigonal pyramid (l), Å	h/l	Deformation of the trigonal pyramid, %
$MgAl_2C_2$	0.594	3.088	3.377	0.914	+11.9	2.729	3.377	0.808	-1.0
$MgAl_2Si_2$	0.906	3.320	4.05	0.820	+0.4	3.420	4.05	0.844	+3.4
$MgAl_2Ge_2$	0.982	3.284	4.117	0.798	-2.3	3.504	4.117	0.851	+4.2
$CaAl_2Si_2$	0.772	3.858	4.130	0.934	+14.4	3.287	4.130	0.796	-2.5
$CaAl_2Ge_2$	0.837	3.754	4.175	0.899	+10.1	3.419	4.175	0.819	+0.3
$SrAl_2Si_2$	0.700	4.092	4.183	0.978	+19.8	3.318	4.183	0.793	-2.9
$SrAl_2Ge_2$ [b]	0.758	...	4.225	...	...	...	4.225	...	...

[a] Covalent radii r_C = 0.813, r_{Si} = 1.239, r_{Ge} = 1.343, r_{Mg} = 1.367, r_{Ca} = 1.604, r_{Sr} = 1.771 Å (octahedral coordination) [14].

[b] Atomic coordinates not refined.

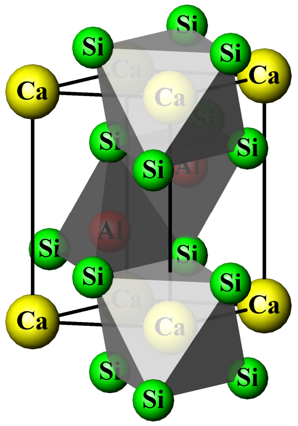


Fig. 3 Structure type $CaAl_2Si_2$ emphasizing $AlSi_4$ trigonal pyramids and $CaSi_6$ trigonal antiprisms.

the covalent radii r_M/r_R for alumosilicides and alumogermanides is shown in Fig. 4. The smallest deformation of the octahedra is observed for the compound $MgAl_2Si_2$, whereas the tetrahedra are almost undistorted for $CaAl_2Ge_2$. The ratios r_M/r_R are in the range 0.700-0.982, and with increasing values the initially elongated trigonal antiprisms become compressed, whereas the initially compressed trigonal pyramids become elongated. The cross-over of the two curves is observed for a deformation of +2.7% and r_M/r_R = 0.889.

The trigonal pyramids are less distorted than the trigonal antiprisms, which is in agreement with the fact that stronger interactions are expected between Al and M atoms. The deviation of the c/a ratio from the ideal value $2(⅔)^{½}$ = 1.6330 is an average between the deformations of the two polyhedra. The z-coordinate of the M atoms shows a stronger dependence on the r_M/r_R ratio, which indicates that larger R atoms push neighboring M layers apart along the direction **c**.

In [15] the character of the chemical bonding in the compound $CaAl_2Si_2$ was estimated based on a refinement of the atomic coordinates and their anharmonic and multipole parameters from high-precision X-ray single-crystal diffraction. Plots of experimental electron density were made and the ionic part of the bonding was determined as $Ca^{1+}Al^{0.25+}{}_2Si^{0.75-}{}_2$.

A crystal-chemical analysis of the structure of the new compound $MgAl_2Ge_2$ was performed. Its trigonal structure can be derived from the hexagonal structure type AlB_2 (space group $P6/mmm$) *via* the hexagonal ZrBeSi and trigonal γ-EuPtP structure types [6] (Fig. 5). The first step is to order the smaller atoms so that short homoatomic distances are avoided; as a consequence the unit cell is doubled along the crystallographic direction [001]. This transformation leads to the realization of the structure type ZrBeSi (space group $P6_3/mmc$). The Be and Si atoms are orderly distributed and between them there are only heteroatomic bonds. Then the structure of ZrBeSi should be slightly deformed, so that the smaller atoms Be (⅓ ⅔ ¼) and Si (⅓ ⅔ ¾) are shifted from the ideal positions in the flat nets along the direction **c**. A particular arrangement of shifts up-down cause a transition to the structure type γ-EuPtP (space group $P\text{-}3m1$), which contains slightly puckered meshes of Pt and P atoms. The Eu atoms occupy the position of the Zr atoms in the structure of ZrBeSi, whereas the Pt (⅓ ⅔ 0.7388) and P (⅓ ⅔ 0.2596) atoms occupy the positions of the Be and Si atoms. Finally, to obtain an atom arrangement similar to that of the type $CaAl_2Si_2$ every second layer of Eu atoms in the structure type γ-EuPtP should be removed. The positions of the Eu atoms that remain correspond to the positions of the Ca atoms in the structure type $CaAl_2Si_2$; the M sites near the vacant Eu layer are occupied by Al atoms, whereas the Si atoms occupy the positions near the remaining Eu layer. The smaller atoms (Al and Si) form puckered meshes in the plane xy so that the Al atoms are in a distorted tetrahedral environment.

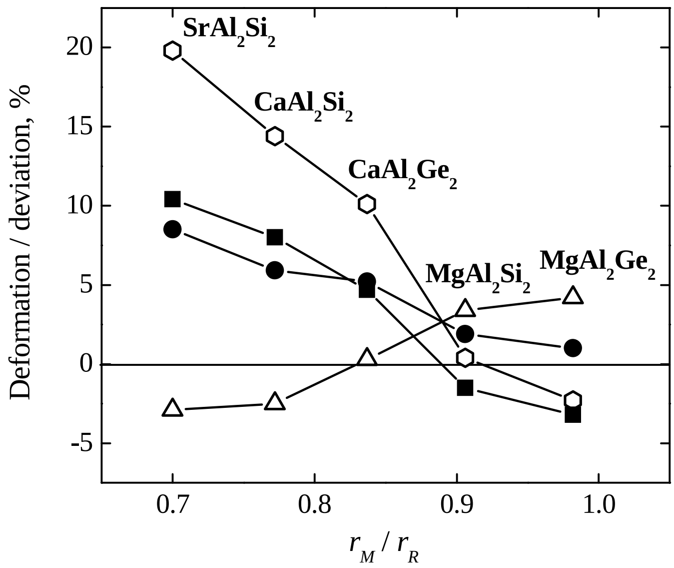
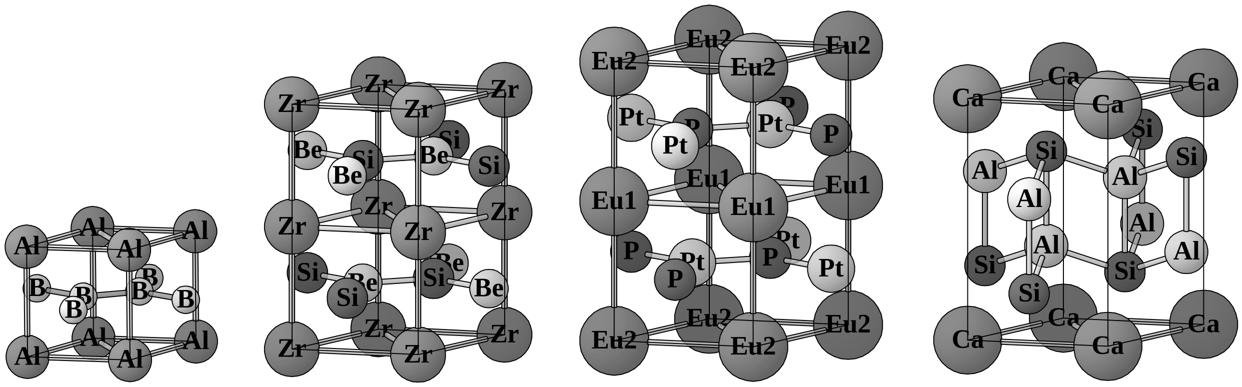


Fig. 4 Deformation of *R*-centered M_6 octahedra (trigonal antiprisms, ⬡) and Al-centered M_4 tetrahedra (trigonal pyramids, △), deviation of the *c*/*a* ratio (●) and *z*-coordinate of the *M*-element atoms (■) from the ideal values for the compounds RAl_2M_2.



AlB_2 (*P*6/*mmm*) ZrBeSi ($P6_3/mmc$) γ-EuPtP (*P*-3*m*1) $CaAl_2Si_2$ (*P*-3*m*1)

Fig. 5 Structures of the types AlB_2, ZrBeSi, γ-EuPtP, and $CaAl_2Si_2$.

Conclusions

The new compound $MgAl_2Ge_2$ is the third representative of the structure type $CaAl_2Si_2$ among alkali-earth alumogermanides RAl_2Ge_2 and the third representative among magnesium aluminides $MgAl_2M_2$ where *M* is a *p*-element of group IV of the periodic system. When the ratio of the covalent atomic radii r_M/r_R increases from 0.700 ($SrAl_2Si_2$) to 0.982 ($MgAl_2Ge_2$), the *R*-centered elongated trigonal antiprisms M_6 become compressed, whereas the Al-centered compressed trigonal pyramids M_4 become elongated. The trigonal structure type $CaAl_2Si_2$ can be derived from the hexagonal structure type AlB_2 *via* the hexagonal type ZrBeSi and the trigonal type γ-EuPtP.

Acknowledgments

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