

Monoclinic La_2AlGe_6 and Isotypes, a Vacancy Variant of the Orthorhombic SmNiGe_3 Type

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Abstract. $\text{La}_2\text{Al}_{1+x}\text{Ge}_{6-x}$ [$x = 0.60(4)$], $M_r = 712.98$, monoclinic, $mS36$, (12) $C2/m - j^2i^5$, $a = 8.373(2)$, $b = 8.833(2)$, $c = 10.887(3)$ Å, $\beta = 101.34(2)^\circ$, $V = 789.4(2)$ Å³, $Z = 4$, $D_x = 5.999$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 32.30$ mm⁻¹, $F(000) = 1230$, $T = 300$ K, $R = 0.040$ and $wR = 0.031$ for 859 contributing unique reflections. Isotypes are found for $R_2\text{Al}_{1+x}\text{Ge}_{6-x}$ with $R = \text{Ce, Pr, Nd, Sm and Gd}$. This new structure type is a vacancy variant of the orthorhombic SmNiGe_3 structure and can be considered as an intergrowth of AlB_2 -, deformed Po- and partially vacant inverse- ThCr_2Si_2 -type slabs. It is a slab stacking variant of the pseudobinary $\text{Ce}_2(\text{Ge}_{0.9}\text{Ge}_{0.1})_7$ type, another vacancy variant of the SmNiGe_3 type.

Introduction. The La-poor part (< 35 at.% La) of the La–Al–Ge ternary phase diagram was investigated by Muravyeva & Zarechnyuk (1970). Of the five compounds reported, the crystal structures of four compounds are known: hexagonal LaAl_2Ge_2 with CaAl_2Si_2 type, hexagonal $\text{LaAl}_{2-x}\text{Ge}_x$ ($0.2 \leq x \leq 0.5$) with AlB_2 type, tetragonal LaAlGe with $\alpha\text{-ThSi}_2$ type (or an ordered variant) and orthorhombic $\text{La}_2\text{Al}_3\text{Ge}_4$ with $\text{Ba}_2\text{Cd}_3\text{Bi}_4$ type. For more details see Zhao & Parthé (1991). Here we report on the structure determination of the fifth compound with nominal composition ‘ LaAlGe_3 ’.

Experimental. A sample of nominal composition ‘ LaAlGe_3 ’ was prepared by arc melting under argon atmosphere (La, Al and Ge: 99.99%). The weight loss was 0.4%. The sample was annealed at 770 K for two months in an Ar-filled silica tube. A regular-shaped single crystal [$\pm(100)$: 0.016, $\pm(010)$: 0.040, $\pm(001)$: 0.016 mm], obtained from the annealed sample, was mounted on a Philips PW1100 automatic four-circle diffractometer; Mo $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 28 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $20 < 2\theta < 40^\circ$) using *LATCON* (Schwarzenbach, 1966). 2660 reflections were collected out to $(\sin\theta/\lambda) = 0.703$ Å⁻¹ ($0 \leq h \leq$

11 , $0 \leq k \leq 12$, $-15 \leq l \leq 15$ and the anti-reflections) in the ω - 2θ scan mode, yielding 1228 unique reflections ($R_{\text{int}} = 0.017$). Two standard reflections ($\bar{2}\bar{2}\bar{1}$ and $0\bar{4}0$) were measured with max. intensity variations 0.6 and 0.4% respectively. Absorption correction was made using *ABSORB* (Davenport, Spadaccini & Stewart, 1990) with max. and min. transmission factors of 0.4068 and 0.2178. The anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Systematic absences led to the following possible space groups: $C2$, Cm and $C2/m$ (*International Tables for Crystallography*, 1983, Vol. A). The structure was solved in space group $C2/m$ using *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). The abnormally high atomic displacement parameters of three Ge sites in the starting refinement indicated that these positions should have some Al atoms substituting for the Ge atoms. The refined composition was confirmed by the microprobe analysis which gave the composition as $\text{La}_{0.20(1)}\text{Al}_{0.17(3)}\text{Ge}_{0.63(2)}$. The full-matrix least-squares refinement was based on $|F|$ values using *CRYLSQ* (Olthof-Hazekamp, 1990). 42 variables, including isotropic and anisotropic atomic displacement parameters, refined to $R = 0.040$ and $wR = 0.031$ [$w = 1/\sigma^2(|F_{\text{rel}}|)$, $S = 1.985$] considering 859 contributing unique reflections with $|F_{\text{rel}}| > 3\sigma(|F_{\text{rel}}|)$. Secondary-extinction correction parameter (Gaussian distribution of mosaic spread) was refined to $G = 0.0195(3)$. The max. shift/e.s.d. in the last cycle was 0.0003. * Final residual electron density $+4.5(-4.1)$ e Å⁻³. The programs used to refine the structure are all from the *XTAL3.0* system (Hall & Stewart, 1990). The atomic positional parameters were standardized by using the *STRUCTURE TIDY* (Gelato & Parthé, 1987) program. The atomic posi-

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54084 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tional and displacement parameters are given in Table 1 and the interatomic distances up to 3.45 Å in Table 2.

Isotypic compounds

The five isotypic $R_2Al_{1+x}Ge_{6-x}$ compounds listed in the *Abstract* and in Table 3 were also prepared by the arc-melting method under Ar atmosphere. The samples were annealed at 773 K for two weeks in an Ar-filled silica tube. The observed powder patterns

Table 1. Atomic positional and displacement parameters for $La_2Al_{1+x}Ge_{6-x}$ [$x = 0.60$ (4)] with space group $C2/m$

The isotropic atomic displacement factors are expressed as $T = \exp[-2\pi^2 U(\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

	Wyckoff position	x	y	z	$U(\text{Å}^2 \times 10^3)$
La	8(j)	0.08527 (8)	0.24828 (9)	0.33612 (6)	0.72 (3)
X(1)	8(j)	0.2783 (2)	0.2131 (1)	0.1125 (1)	1.10 (4)*
X(2)	4(i)	0.0694 (3)	0	0.1123 (2)	1.01 (7)*
Ge(1)	4(i)	0.1460 (3)	0	0.5640 (2)	0.96 (9)
Ge(2)	4(i)	0.3597 (3)	0	0.4195 (2)	1.15 (9)
X(3)	4(i)	0.4869 (3)	0	0.1133 (2)	1.23 (7)*
Al	4(i)	0.8006 (7)	0	0.1952 (5)	1.3 (2)

Site occupancy: $X(1) = Ge_{0.91(1)}Al_{0.09(1)}$; $X(2) = Ge_{0.77(1)}Al_{0.23(1)}$; $X(3) = Ge_{0.81(1)}Al_{0.19(1)}$.

* Atomic displacement parameters refined isotropically.

Table 2. Interatomic distances up to 3.45 Å in $La_2Al_{1+x}Ge_{6-x}$ [$x = 0.60$ (4)]

La—	Ge(2)	3.164 (2)	Ge(1)—	Ge(1)	2.566 (3)
	Ge(2)	3.177 (2)		Al	2.571 (6)
	X(1)	3.191 (2)		Ge(2)	2.605 (3)
	X(1)	3.192 (2)		2La	3.198 (2)
	Ge(1)	3.198 (2)		2La	3.251 (2)
	Ge(1)	3.251 (2)		2La	3.275 (2)
	X(2)	3.261 (2)	Ge(2)—	Ge(1)	2.605 (3)
	Ge(1)	3.275 (2)		Ge(2)	2.641 (3)
	X(3)	3.275 (2)		2La	3.164 (2)
	Al	3.377 (4)		2La	3.177 (2)
	Al	3.411 (5)		2La	3.428 (2)
	Ge(2)	3.428 (2)			
X(1)—	X(1)	2.490 (2)	X(3)—	X(3)	2.518 (3)
	X(3)	2.567 (2)		2X(1)	2.567 (2)
	X(2)	2.569 (2)		Al	2.602 (6)
	Al	2.684 (2)		2La	3.275 (2)
	La	3.191 (2)	Al—	Ge(1)	2.571 (6)
	La	3.192 (2)		X(2)	2.584 (2)
X(2)—	X(2)	2.493 (3)		X(3)	2.602 (6)
	2X(1)	2.569 (2)		2X(1)	2.684 (2)
	Al	2.584 (7)		2La	3.377 (4)
	2La	3.261 (2)		2La	3.411 (5)

Table 3. Unit-cell parameters for $La_2Al_{1+x}Ge_{6-x}$ and its isotypes

Compound	E.s.d.'s are given in parentheses					
	x	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
La ₂ Al _{1+x} Ge _{6-x}	0.60 (4)	8.373 (2)	8.833 (2)	10.887 (3)	101.34 (2)	789.4 (2)
Ce ₂ Al _{1+x} Ge _{6-x}		8.292 (2)	8.691 (1)	10.739 (3)	101.15 (2)	759.3 (2)
Pr ₂ Al _{1+x} Ge _{6-x}		8.244 (4)	8.630 (4)	10.711 (5)	101.09 (4)	747.8 (4)
Nd ₂ Al _{1+x} Ge _{6-x}		8.220 (5)	8.623 (5)	10.671 (5)	101.05 (8)	742.4 (8)
Sm ₂ Al _{1+x} Ge _{6-x}		8.105 (1)	8.458 (1)	10.613 (2)	101.00 (2)	714.2 (2)
Gd ₂ Al _{1+x} Ge _{6-x}		8.041 (3)	8.351 (5)	10.546 (3)	100.81 (3)	695.5 (5)

were compared with simulated powder diagrams calculated using *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). The unit-cell parameters for the $R_2Al_{1+x}Ge_{6-x}$ phases isotypic with $La_2Al_{1+x}Ge_{6-x}$ were refined from either single-crystal data ($R = Ce, Pr$ and Sm) or Guinier film data ($R = Nd$ and Gd) of the annealed samples. The single-crystal data were measured and refined by using the same method as for the $La_2Al_{1+x}Ge_{6-x}$ crystal. No efforts were made to determine the homogeneity range for any of the isotypic phases. The films were measured with a film reader using an internal Si standard ($a = 5.4308$ Å) and *LATCON* (Schwarzenbach, 1966) was used for the refinement.

Discussion. The $La_2Al_{1+x}Ge_{6-x}$ structure is a slightly distorted vacancy variant of the $SmNiGe_3$ type (Bodak, Pecharskii, Mruz, Zavodnik, Vitvits'kaya & Salamakha, 1985) or its lower symmetry variant, the $ScNiSi_3$ type (Kotur, Bodak, Mys'kiv & Gladyshevskii, 1977). To understand the construction of the $La_2Al_{1+x}Ge_{6-x}$ structure and its relation to the $SmNiGe_3$ type, it is convenient to discuss first the $SmNiGe_3$ structure, shown in a projection along [001] on the left-hand side of Fig. 1(a). This structure (or $ScNiSi_3$) can be considered as an intergrowth of three different kinds of slabs (Grin', Yarmolyuk & Gladyshevskii, 1982):

(a) The Po-type slabs are built up of Ge atoms only.

(b) The inverse- $ThCr_2Si_2$ -type slabs formed with rare-earth, Ni and Ge atoms, are built up as the $ThCr_2Si_2$ -type slabs but with Cr and Si sites having been interchanged.* The Ni atoms are at the centres of the compressed square antiprisms of composition Sm_4Ge_4 . The upper and lower interfaces of the inverse- $ThCr_2Si_2$ -type slab are different. The one

* The term 'inverse- $ThCr_2Si_2$ -type' has been applied to $CaZn_2Al_2$ (Cordier, Czech & Schäfer, 1984) where the Al atoms occupy the tetrahedral Cr sites (corresponding sites in inverse- $ThCr_2Si_2$ -type slabs will be referred to as t sites hereafter) and Zn the square antiprismatic Si sites (a sites). No ternary rare-earth-transition-metal silicide or germanide structures are known which are built up exclusively of inverse- $ThCr_2Si_2$ -type slabs; however, it is possible to have an intergrowth with their rare-earth interfaces of a regular and an inverse- $ThCr_2Si_2$ -type slab, e.g. in $LaIr_2Si_2$ HT (Braun, Engel & Parthé, 1983) with $CaBe_2Ge_2$ type. Inverse- $ThCr_2Si_2$ -type slabs are observed in many other intergrowth structures.

consisting of rare-earth atoms acts as interface for an intergrowth with the AlB_2 -type slab, while the other one, consisting of Ge atoms, serves as common interface with the Po-type slab.

(c) The AlB_2 -type slabs consists of Sm and Ge atoms with the Ge atoms at the centres of the trigonal rare-earth prisms.

In one unit cell of $SmNiGe_3$ eight slabs are intergrown along [010] in the sequence:

Po-inverse- $ThCr_2Si_2$ - AlB_2 -inverse- $ThCr_2Si_2$ -Po-inverse- $ThCr_2Si_2$ - AlB_2 -inverse- $ThCr_2Si_2$.

Two vacancy variants of the $SmNiGe_3$ type have been reported. The first was found for Ce_2CuGe_6 (Konyk, Salamakha, Bodak & Pecharskii, 1988) which is shown in a projection along [100] on the right-hand side of Fig. 1(a). As was pointed out by Pani & Fornasini (1990) this structure can be considered as an intergrowth of four different kinds of slabs along [001] in the sequence Po- CaF_2 - AlB_2 -inverse- $ThCr_2Si_2$ -Po- CaF_2 - AlB_2 -inverse- $ThCr_2Si_2$.^{*} The new CaF_2 -type slab is actually an inverse-

^{*} In the paper of Pani & Fornasini (1990) the inverse- $ThCr_2Si_2$ -type slab was labelled $BaAl_4$ -type slab which is an equivalent formulation because the $ThCr_2Si_2$ type is a substitution derivative of the $BaAl_4$ type. The CaF_2 -type slab was cited as $ZrSi_2$ segment by Konyk *et al.* (1988), $ZrSi_2$ being an intergrowth of CaF_2 - and AlB_2 -type slabs.

$ThCr_2Si_2$ -type slab where the atoms on the a sites have been completely removed.

The second vacancy variant of the $SmNiGe_3$ type has been reported for the pseudobinary compound $Ce_2(Ge_{0.9}Ga_{0.1})_7$ with space group $Cmca$ (Yarmolyuk, Pecharskii, Gryniv, Bodak & Zavodnik, 1989), for which half of its unit cell ($0 \leq x < \frac{1}{2}$) is shown in a projection along [100] on the left-hand side of Fig. 1(b). The atom arrangement in the other half of the unit cell ($\frac{1}{2} \leq x < 1$) is identical to the one shown except for a shift by $\frac{1}{2}b$, as required by the C-Bravais lattice. Owing to the ordering of the vacancies the b and a vectors of $Ce_2(Ge_{0.9}Ga_{0.1})_7$ are twice as long as the corresponding a and c vectors of $SmNiGe_3$. The $Ce_2(Ge_{0.9}Ga_{0.1})_7$ structure can also be considered as an intergrowth of three kinds of slabs along the [001] direction:

(a) The Po-type slabs are deformed and built up of X atoms ($X = Ge_{0.9}Ga_{0.1}$).

(b) The $Ba[]Al_3$ -type slabs, containing rare earth and X atoms, have completely ordered vacancies. The square antiprism of composition Ce_4X_4 around the central X atom (being not on the interface with the Po-type slab) is expanded due to the X -atom displacements on the interface.

(c) The AlB_2 -type slabs also consist of Ce and X atoms with the X atoms at the centres of the trigonal

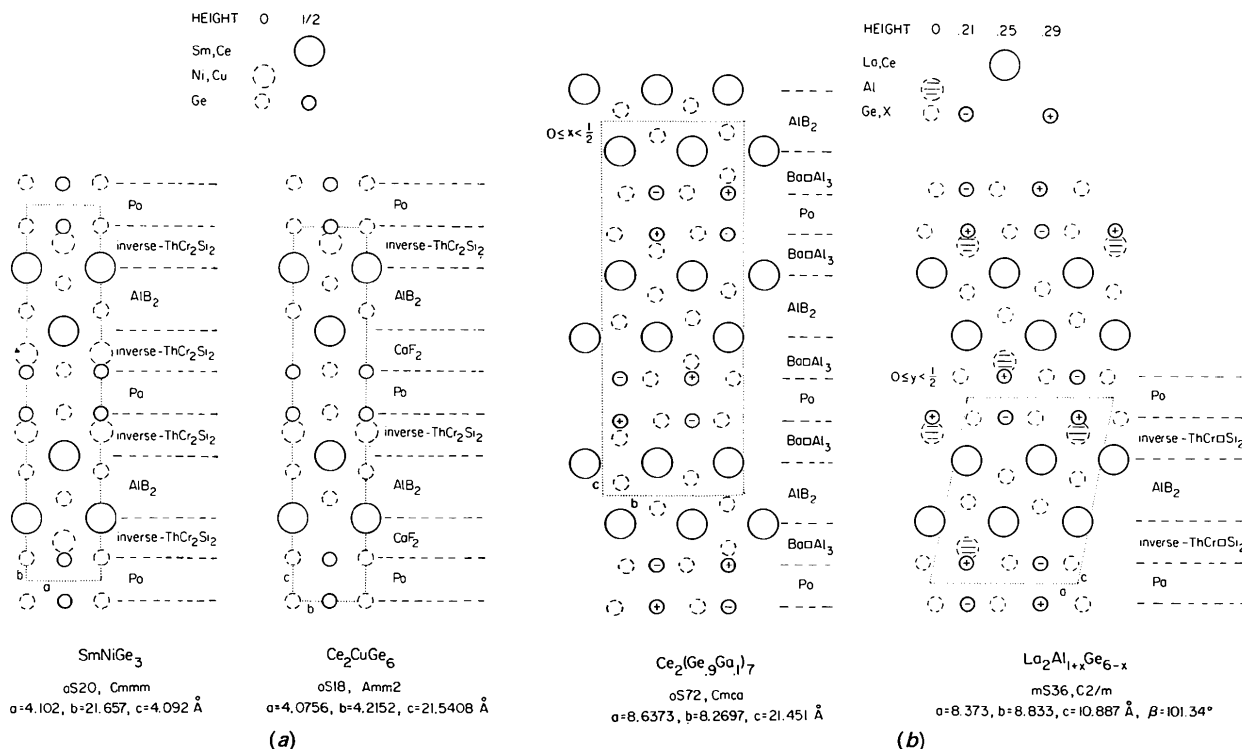


Fig. 1. (a) Projections of $SmNiGe_3$ along direction [001] and of Ce_2CuGe_6 along [100]. Slabs of parent types which are used to build these structures are indicated beside the drawings. (b) Projections of $Ce_2(Ge_{0.9}Ga_{0.1})_7$ along [100] for $0 \leq x < \frac{1}{2}$ and of $La_2Al_{1-x}Ge_{6-x}$ along [010] for $0 \leq y < \frac{1}{2}$. Slabs of parent types which are used to build these structures are indicated beside the drawings. The $BaAl_4$ -type slabs with vacancies are denoted as $Ba[]Al_3$, and the inverse- $ThCr_2Si_2$ -type slabs with vacancies as inverse- $ThCr[]Si_2$.

Ce prisms. The *X* atoms are slightly displaced from their ideal positions.

In one unit cell the slabs are stacked in the sequence Po–Ba[]Al₃–AlB₂–Ba[]Al₃–Po–Ba[]Al₃–AlB₂–Ba[]Al₃.

The new La₂Al_{1+x}Ge_{6-x} structure is also a vacancy variant of the SmNiGe₃ structure, and the vacancies are also regularly distributed over all inverse-ThCr₂Si₂-type slabs. A projection of the La₂Al_{1+x}Ge_{6-x} structure along [010] for half of one unit cell ($0 \leq y < \frac{1}{2}$) is shown on the right-hand side of Fig. 1(b). The atom arrangement in the other half of the unit cell ($\frac{1}{2} \leq y < 1$) is identical, except for a shift by $\frac{1}{2}\mathbf{a}$, as required by the *C*-Bravais lattice. Also here the ordering of the vacancies leads to a doubling of the *a* and *b* vectors as compared to the corresponding *a* and *c* vectors of SmNiGe₃. One recognizes that the La₂Al_{1+x}Ge_{6-x} structure can be considered as an intergrowth of three kinds of slabs:

(a) The Po-type slabs are deformed and built up of *X* atoms [*X*(1), *X*(2) and *X*(3)], *i.e.* Ge atoms partially substituted by Al atoms.

(b) The inverse-ThCr[]Si₂-type slabs have rare-earth atoms, aluminium atoms on *a* sites and *X* atoms (essentially Ge with a small substitution of Al) on *t* sites. In the slabs only one of two possible *a* sites is occupied, the vacancies being arranged in an ordered way. The *X* atoms are slightly displaced from their ideal *t* sites so that they are closer to an unoccupied *a* site and further away from an occupied *a* site which leads to an expanded square antiprism of composition La₄X₄ around the Al atom.

(c) The AlB₂-type slabs consist only of La, Ge(1) and Ge(2) atoms with the Ge atoms at the centres of the trigonal La prisms. The Ge atoms are slightly displaced from their ideal positions.

In one monoclinic unit cell of La₂Al_{1+x}Ge_{6-x} four slabs are intergrown along the direction perpendicular to the (001) plane. Their stacking sequence is Po–inverse-ThCr[]Si₂–AlB₂–inverse-ThCr[]Si₂.

As a consequence of the deformations with respect to the SmNiGe₃ type, observed essentially in the planes forming the Po-type slab, the coordination of the sites forming these planes has been modified. It can be seen from Table 2 that sites *X*(1), *X*(2) and *X*(3) are all surrounded by four small atoms (3*X* + 1 Al), a coordination which should be compared to the environment of the corresponding Ge site in SmNiGe₃ (2 Ni + 5 Ge). The coordination of the Al site, ignoring contacts with rare-earth atoms, is a square pyramid (1 Ge + 4*X*), similar to that of the Ni site in SmNiGe₃ (5 Ge) and of the corresponding site in ThCr₂Si₂.

The Ce₂(Ge_{0.9}Ga_{0.1})₇ and La₂Al_{1+x}Ge_{6-x} structures can be considered as slab stacking variants. Fig. 2 demonstrates schematically how the monoclinic La₂Al_{1+x}Ge_{6-x} type (cell vectors *a*_M, *b*_M, *c*_M)

can be obtained from the orthorhombic Ce₂(Ge_{0.9}Ga_{0.1})₇ type (cell vectors *a*_O, *b*_O, *c*_O) by slicing the latter along the (001) planes and shifting successive slabs by $\frac{1}{2}\mathbf{b}_O$. The new atom arrangement, which corresponds to the La₂Al_{1+x}Ge_{6-x} type, can be described with the monoclinic cell shown with dotted lines. For the idealized structures the following relations can be derived from Fig. 2 (ignoring the origin shift): $\mathbf{a}_O = \mathbf{b}_M$, $\mathbf{b}_O = -\mathbf{a}_M$ and $\mathbf{c}_O = \frac{1}{2}\mathbf{a}_M + 2\mathbf{c}_M$ and further $\sin(\beta_M - 90^\circ) = |\mathbf{a}_M|/4 \cdot |\mathbf{c}_M|$.

Inverse-ThCr[]Si₂ slabs with an ordered vacancy arrangement (requiring a doubling of two translation periods) have also been observed in Lu₅Co₄Si₁₄ (Chabot & Parthé, 1986) and Y₉Os₄Si₂₀ (Gueramian, Chabot, Yvon, Schellenberg & Braun, 1988) with Co or Os atoms centring the Lu(Y)₄Si₄ square antiprisms. In both structures these slabs are intergrown with AlB₂-type slabs, as in La₂Al_{1+x}Ge_{6-x}, and with slabs of a third kind. The deformation features of the inverse-ThCr[]Si₂-type slabs in these two silicides are similar to those observed in the La₂Al_{1+x}Ge_{6-x} structure, *i.e.* the Si atoms have moved closer to an unoccupied *a* site and further away from an occupied *a* site. Disordered vacancies on *a* sites in inverse-ThCr₂Si₂-type slabs have been reported for several intergrowth structures, as for example Sm₄Co_{1-x}Ge₇

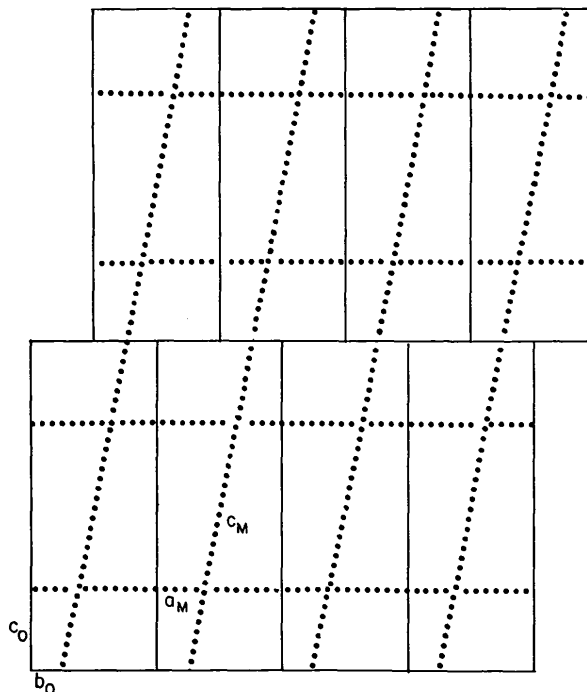


Fig. 2. Schematic slab stacking relation between the monoclinic La₂Al_{1+x}Ge_{6-x} type (cell vectors *a*_M, *b*_M, *c*_M) and the orthorhombic Ce₂(Ge_{0.9}Ga_{0.1})₇ type (cell vectors *a*_O, *b*_O, *c*_O). By slicing the latter along the (100) planes and shifting successive slabs for $\frac{1}{2}\mathbf{b}_O$, the new atom arrangement corresponds to the La₂Al_{1+x}Ge_{6-x} type. Its monoclinic translation lattice is shown with dotted lines.

(Mruz, Pecharskii, Bodak & Bruskov, 1987) or CeNiSi₂ (Dörrscheidt, Savelsberg, Stöhr & Schäfer, 1982; Chabot, Parthé & Steinmetz, 1986; François, Venturini, Malaman & Roques, 1990; Venturini, François, Malaman & Roques, 1990).

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La₂Al₃Ge₄ and Isotypes of the Orthorhombic Ba₂Cd₃Bi₄ Type, a Slab-Stacking Variant of the HfFe₂Si₂ Type

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Abstract. La₂Al₃Ge₄, $M_r = 649.125$, orthorhombic, Ba₂Cd₃Bi₄ type, $oS36$, (64) $Cmca - f^2e^2a$, $a = 6.146$ (2), $b = 15.194$ (4), $c = 8.037$ (2) Å, $V = 750.4$ (2) Å³, $Z = 4$, $D_x = 5.745$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 28.318$ mm⁻¹, $F(000) = 1124$, $T = 300$ K, $wR = 0.036$ for 472 contributing unique reflections. Isotypes are found for R₂Al₃Ge₄ with R = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er. The Ba₂Cd₃Bi₄ type together with a branch, called the Hf₂Ni₃Si₄ type, can be considered as a slab-stacking variant of the HfFe₂Si₂ type. The change of stoichiometry from HfFe₂Si₂ to Hf₂Ni₃Si₄ is caused by the

coalescing of two different Fe sites at the stacking border.

Introduction. The La-deficient part (< 35 at.% La) of the La–Al–Ge ternary phase diagram was investigated by Muravyeva & Zarechnyuk (1970). Three crystal structures of the five compounds reported had been known: LaAl₂Ge₂ has the CaAl₂Si₂ type (*anti*-Ce₂O₂S type) (Zarechnyuk, Muravyeva & Gladyshevskii, 1970), LaAl_{2-x}Ge_x (0.2 ≤ x ≤ 0.5) crystallizes with the AlB₂ type (Raman & Steinfink, 1967) and LaAlGe with the α-ThSi₂ type (or an ordered