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# Quaternary alumogermanides in the Er-{Co,Ni}-Al-Ge systems

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**The crystal structures of two new quaternary alumogermanides have been determined from X-ray single crystal and powder diffraction data. $Er_2CoAl_4Ge_2$ crystallizes with a $Tb_2NiAl_4Ge_2$-type structure: space group *I*4/*mmm*, Pearson symbol *tI*18, cell parameters *a* = 4.0970(6), *c* = 19.343(4) Å, *R*1 = 0.0492, *wR*2 = 0.1195, *Goof* = 1.115, whereas the structure of $ErNiAl_4Ge_2$ adopts the $YNiAl_4Ge_2$ type: space group $R\bar{3}m$, Pearson symbol *hR*24, cell parameters *a* = 4.07160(8), *c* = 30.7027(9) Å, $R_p$ = 0.0550, $R_{wp}$ = 0.0708, $R_B$ = 0.0523, $R_F$ = 0.0402, $\chi^2$ = 3.54. The structures are ordered and built up from structural slabs characteristic of binary and ternary compounds *via* intergrowth.**

**Rare-earth alumogermanides / Crystal structure / X-ray diffraction**

## Introduction

One of the modern trends in chemistry of inorganic materials is the investigation of multicomponent systems. A large number of multicomponent compounds have already been synthesized, however, the number is still small with respect to the number of binary and ternary compounds investigated up to now. Multinary intermetallics containing aluminum are important phases found in many advanced alloys such as aluminum matrix composites. These phases are responsible for the interesting properties of these alloys, but can also cause undesirable effects in certain cases. Detailed knowledge of the composition and crystal structure of the phases formed in multicomponent Al-containing systems is important for the development of new materials with specific properties.

In the present paper we report on the formation of two new alumogermanides, which crystallize with the $Tb_2NiAl_4Ge_2$ [1] and $YNiAl_4Ge_2$ [2] structure types, respectively. The crystal structures of these compounds were solved and refined from X-ray single crystal and powder diffraction data from single-phase samples obtained during systematic investigations of the Er-{Co,Ni}-Al-Ge systems [3-5].

## Experimental

The samples used for the investigation were prepared by melting the elements (purity better than 99.9%) on a water-cooled copper bottom under argon atmosphere (Ti-getter) in an electric arc furnace, and annealed at 870 K for 4 weeks.

X-ray powder patterns were recorded at room temperature using a DRON-2.0M powder diffractometer with Fe *K*α radiation. The measurements were carried out in 2$\theta$ steps of 0.02° with a scan time of 1.5 s.

A single crystal of prismatic shape of $Er_2CoAl_4Ge_2$ was extracted from an alloy of nominal composition $Er_{17.7}Co_{17.7}Al_{46.9}Ge_{17.7}$. A preliminary investigation was performed using Laue and rotation methods (RKV-86 and RGNS-2 chambers, Mo *K*α radiation). Intensity data were collected on an automatic single-crystal diffractometer Enraf-Nonius CAD4 (Cu *K*α radiation, $\lambda$ = 1.54184 Å, graphite monochromator, $\omega/2\theta$-scan) using the program SDP [6]. The program EAC [7] was used to apply an empirical absorbtion correction ($\psi$-scan). The crystal structure was solved by direct methods and refined with the SHELX-97 program package [8].

The crystal structure of $ErNiAl_4Ge_2$ was refined from powder diffraction data with the program FullProf.2k (version 4.00) [9] from the WinPLOTR software [10], using a pseudo-Voigt profile function. The refinement procedure was begun with the zero correction, scale factor and profile shape parameters. The cell parameters, peak FWHM and asymmetry parameters were included at the next steps. After that, the atomic positions and isotropic displacement parameters were allowed to vary and, finally, all parameters were refined together. Preferred orientation was observed and a texture parameter was refined. A second refinement of the structure of $Er_2CoAl_4Ge_2$ was performed in a similar way on powder diffraction data.

The crystallographic data were standardized with the program Structure Tidy [11].

## Results and discussion

Experimental and crystallographic data for $Er_2CoAl_4Ge_2$ and $ErNiAl_4Ge_2$ are given in Tables 1 and 2, while the final atomic and displacement parameters are listed in Tables 3 and 4. Interatomic distances and coordination numbers are given in Table 5. Comparisons of experimental and calculated powder patterns are presented in Figs. 1 and 2. The crystal structures are isotypic with those of $Tb_2NiAl_4Ge_2$ [1] and $YNiAl_4Ge_2$ [2].

The structure of $Er_2CoAl_4Ge_2$ ($Tb_2NiAl_4Ge_2$ type) can be described as a stacking of 6.374 Å thick $[CoAl_4Ge_2]^{6-}$ slabs, analogous to the $[NiAl_4Ge_2]^{6-}$ slabs emphasized in $Tb_2NiAl_4Ge_2$ [1], and double triangle-mesh $Er^{3+}$ layers. Focusing on the coordination polyhedra, the structure belongs to class #9 (coordination number 8÷10 for the smaller atoms) according to the classification scheme proposed by Kripyakevich [12], since the coordination polyhedron of the Ge site is a square antiprism with one capping atom. Four Al atoms at 2.796 Å and four Er atoms at 2.923 Å form the two square faces of the polyhedron, and an additional Er atom at 2.912 Å caps the $[Er_4]$ face of the antiprism. As shown in Fig. 3, the structure can be considered as a packing of monocapped square antiprisms [**Ge**$Al_4Er_5$] with filled [**Co**$Al_8$] and empty [□$Al_8$] cubes. The eight Al atoms forming the cube around Co are situated at 2.418 Å from the central atom.

**Table 1** Experimental details (single-crystal diffraction) and crystallographic data for $Er_2CoAl_4Ge_2$.

| | |
|---|---|
| Compound | $Er_2CoAl_4Ge_2$ |
| Structure type | $Tb_2NiAl_4Ge_2$ |
| Pearson symbol, $Z$ | *tI*18, 2 |
| Space group – Wyckoff sequence | *I*4/*mmm* – $ge^2a$ |
| Molecular mass (g mol$^{-1}$) | $M_r$ = 646.55 |
| Cell parameters (Å) | $a$ = 4.0970(6), $c$ = 19.343(4) |
| Cell volume (Å$^3$) | 324.68(9) |
| Crystal size (mm) | 0.08 × 0.06 × 0.02 |
| Crystal color | Metallic dark grey |
| Absorption coefficient (mm$^{-1}$) | $\mu$(Cu $K\alpha$) = 80.117 |
| $F$(000) | 558 |
| Angular range for data collection (°) | 4.57 ≤ $\theta$ ≤ 74.31 |
| Limiting indices | -5 ≤ $h$ ≤ 0, -5 ≤ $k$ ≤ 5, -24 ≤ $l$ ≤ 24 |
| Reflections collected / unique | 774 / 135 ($R_{int}$ = 0.1127) |
| Completeness to $\theta$ = 74.31° | 100% |
| Absorption correction | Empirical, $\psi$-scan method |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 135 / 0 / 14 |
| Goodness-of-fit on $F^2$ | 1.115 |
| Reliability factors ($I > 2\sigma(I)$) | $R$1 = 0.0492, $wR$2 = 0.1195 |
| Reliability factors (all data) | $R$1 = 0.0506, $wR$2 = 0.1212 |
| Extinction coefficient | 0.0008(3) |
| Largest difference peak / hole (e Å$^{-3}$) | 4.464 / -2.778 |

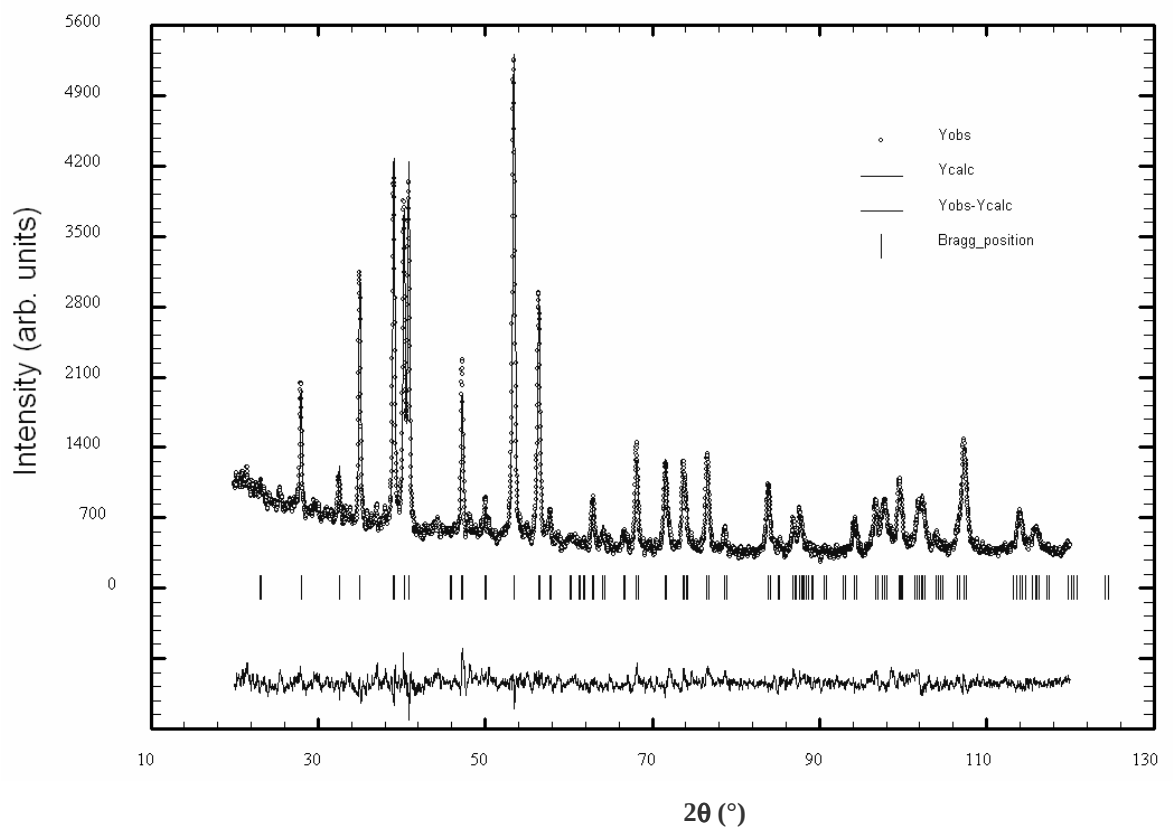


**Fig. 1** Observed and calculated X-ray powder profiles for $Er_2CoAl_4Ge_2$ (Fe *K*α radiation).

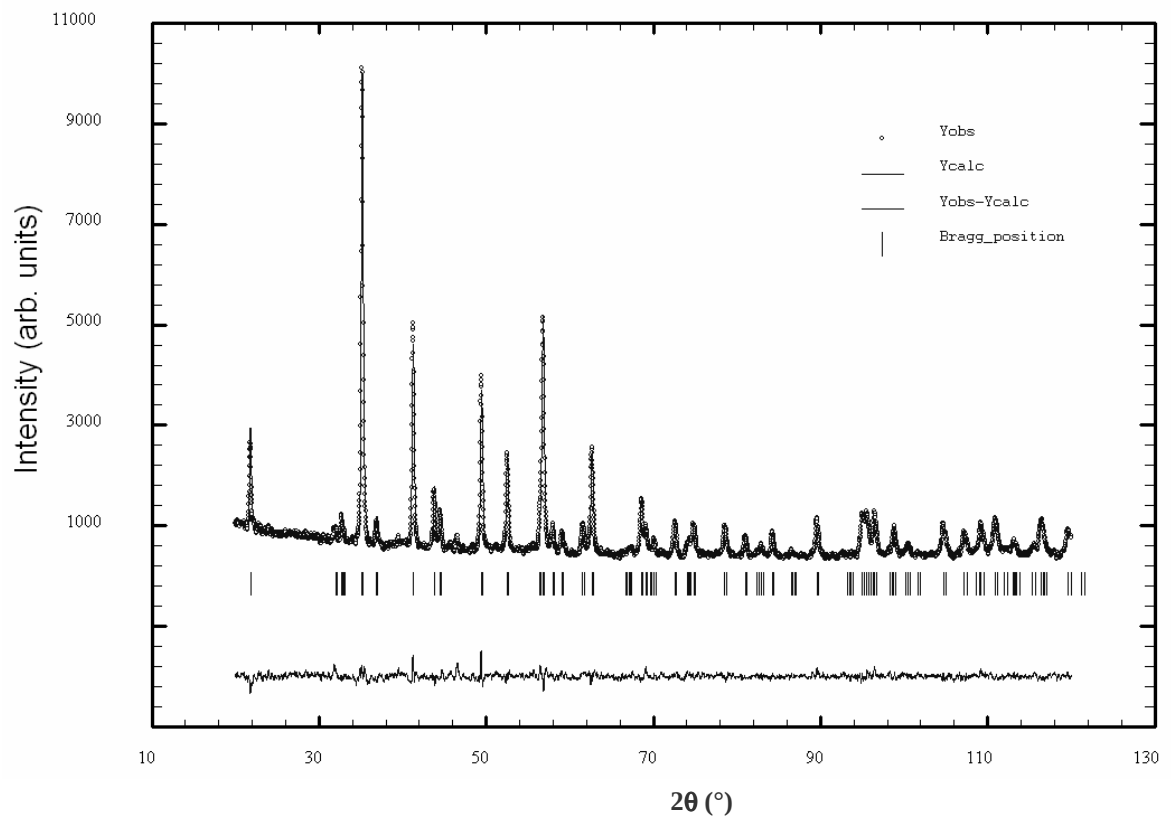


**Fig. 2** Observed and calculated X-ray powder profiles for $ErNiAl_4Ge_2$ (Fe *K*α radiation).

**Table 2** Experimental details (powder diffraction) and crystallographic data for $Er_2CoAl_4Ge_2$ and $ErNiAl_4Ge_2$.

| Compound | $Er_2CoAl_4Ge_2$ | $ErNiAl_4Ge_2$ |
|---|---|---|
| Structure type | $Tb_2NiAl_4Ge_2$ | $YNiAl_4Ge_2$ |
| Pearson symbol, *Z* | *tI*18, 2 | *hR*24, 3 |
| Space group – Wyckoff sequence | $I4/mmm - ge^2a$ | $R\bar{3}m - c^3ba$ |
| Cell parameters (Å) | $a$ = 4.09713(13) | $a$ = 4.07160(8) |
| | $c$ = 19.3310(8) | $c$ = 30.7027(9) |
| Cell volume (Å$^3$) | 324.50(2) | 440.80(2) |
| Angular range for data collection (°) | $20 \le 2\theta \le 120$ | $20 \le 2\theta \le 120$ |
| Number of measured reflections | 116 | 130 |
| Number of refined parameters | 24 | 25 |
| Half width parameters *U*, *V*, *W* | 0.19(2), -0.00(2), 0.050(6) | 0.116(9), -0.04(1), 0.069(3) |
| Texture axis, parameter | [100], 0.141(5) | [110], 0.142(5) |
| Reliability factors: | | |
| $R_B = \Sigma\|I_{obs} - I_{calc}\| / \Sigma\|I_{obs}\|$ | 0.0765 | 0.0523 |
| $R_F = \Sigma\|F_{obs} - F_{calc}\| / \Sigma\|F_{obs}\|$ | 0.0594 | 0.0402 |
| $R_p = \Sigma\|y_i - y_{c,i}\| / \Sigma y_i$ | 0.0613 | 0.0550 |
| $R_{wp} = [\Sigma w_i \|y_i - y_{c,i}\|^2 / \Sigma w_i y_i^2]^{1/2}$ | 0.0787 | 0.0708 |
| $R_{exp} = [n\text{-}p / \Sigma w_i y_i^2]^{1/2}$ | 0.0391 | 0.0376 |
| $\chi^2 = \{R_{wp}/R_{exp}\}^2$ | 4.06 | 3.54 |

**Table 3** Atomic positional and displacement parameters for $Er_2CoAl_4Ge_2$, space group *I*4/*mmm*.

| Site | Wyckoff | *x* | *y* | *z* | $U_{eq}$[a]/$B_{iso}$ (Å$^2$) | $U_{11}$ (Å$^2$) | $U_{22}$ (Å$^2$) | $U_{33}$ (Å$^2$) |
|---|---|---|---|---|---|---|---|---|
| Er | 4*e* | 0 | 0 | 0.18469(7) | 0.0078(7) | 0.0092(8) | 0.0092(8) | 0.0052(10) |
| | | | | *0.18516(9)*[b] | *0.49(5)* | | | |
| Co | 2*a* | 0 | 0 | 0 | 0.0061(12) | 0.008(2) | 0.008(2) | 0.002(2) |
| | | | | | *0.98(15)* | | | |
| Al | 8*g* | 0 | ½ | 0.0664(2) | 0.0091(14) | 0.010(3) | 0.012(3) | 0.005(2) |
| | | | | *0.0657(4)* | *1.3(1)* | | | |
| Ge | 4*e* | 0 | 0 | 0.33523(15) | 0.0080(9) | 0.0103(11) | 0.0103(11) | 0.004(2) |
| | | | | *0.3357(2)* | *1.26(9)* | | | |

[a] $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor. The anisotropic displacement factor exponent takes the form $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$, $U_{12} = U_{13} = U_{23} = 0$.

[b] Values refined on powder diffraction data are in italics.

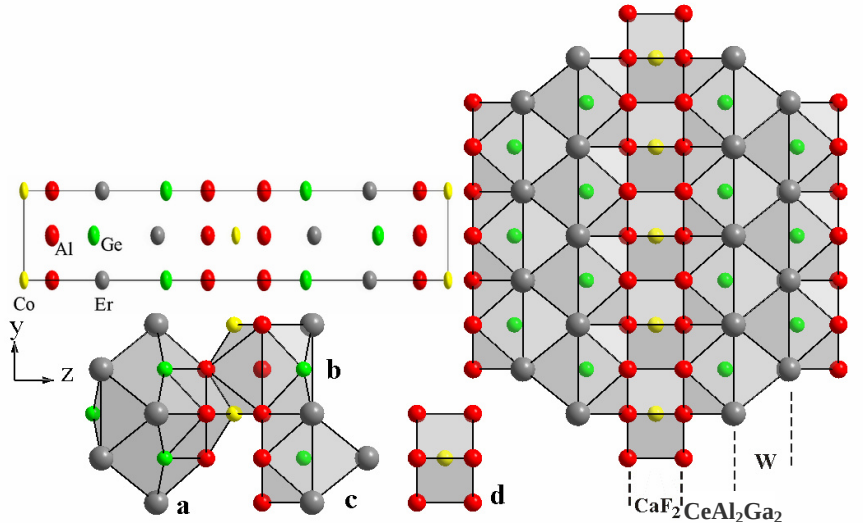


**Fig. 3** Projection of the unit cell of $Er_2CoAl_4Ge_2$ on the (100) plane with displacement ellipsoids, the coordination polyhedra around Er (a – [**Er**$Ge_5Al_4CoEr_8$]), Al (b – [**Al**$Co_2Al_5Ge_2Er_2$]), Ge (c – [**Ge**$Al_4Er_5$]), Co (d – [**Co**$Al_8$]), and packing of monocapped square antiprisms [**Ge**$Al_4Er_5$], filled [**Co**$Al_8$] and empty [□$Al_8$] cubes.

**Table 4** Atomic positional and displacement parameters for $ErNiAl_4Ge_2$, space group $R\bar{3}m$.

| Site | Wyckoff | *x* | *y* | *z* | $B_{iso}$ (Å$^2$) |
|---|---|---|---|---|---|
| Er | 3*b* | 0 | 0 | ½ | 0.55(5) |
| Ni | 3*a* | 0 | 0 | 0 | 0.90(8) |
| Al1 | 6*c* | 0 | 0 | 0.0779(2) | 1.23(12) |
| Al2 | 6*c* | 0 | 0 | 0.3099(2) | 0.78(11) |
| Ge | 6*c* | 0 | 0 | 0.22290(5) | 1.07(7) |

The coordination polyhedron of the Al atoms is an 11-vertex polyhedron with two Co at 2.418 Å, one Al at 2.569 Å, two Ge at 2.796 Å, four additional Al at 2.897 Å, and two Er at 3.071 Å. The Er atoms are surrounded by 18 atoms: four Ge, four Al, and four Er (at 2.923, 3.071, and 3.844 Å, respectively), an additional Ge at 2.912 Å, a Co atom at 3.572 Å, and four additional Er at 4.097 Å.

The structure of $Er_2CoAl_4Ge_2$ can also be described as an intergrowth of slabs characteristic of the simple structure types $CeAl_2Ga_2$, W, and $CaF_2$ along [001]. Examples of structure types built up of intergrown $CeAl_2Ga_2$- and W-type, or $CeAl_2Ga_2$- and $CaF_2$-type slabs are discussed in [13]. The square antiprisms forming the $CeAl_2Ga_2$-type slabs have the composition [**Ge**$Al_4Er_4$] (capping atom ignored). It may be noticed that the $CeAl_2Ga_2$ type has not been observed in the Er-Al-Ge system, but $ErCo_2Ge_2$ adopts this type [14]. [**Co**$Al_8$] cubes, which alternate with empty [□$Al_8$] cubes in the $CaF_2$-type slabs, are found in CoAl, which crystallizes with CsCl-type structure.

An isostructural compound $Er_2NiAl_4Ge_2$ (*I*4/*mmm*, $a$ = 4.1079(6), $c$ = 19.212(4) Å) was observed during our investigation of the system Er-Ni-Al-Ge [5], but could so far not be obtained in pure form.

The crystal structures of $YNiAl_4Ge_2$ and $SmNiAl_4Ge_2$ were determined in [2] from X-ray single-crystal data. The structure is described as an intergrowth of approximately 8 Å-thick $[NiAl_4Ge_2]^{3-}$ slabs formed by seven layers of Al and Ge atoms in the stacking sequence Ge-Al-Al-Ni-Al-Al-Ge (ABABCBC), and close-packed layers of $Y^{3+}$ (or $Sm^{3+}$) ions. An isostructural compounds *RE*$AuAl_4Ge_2$ were found in [15]. $ErNiAl_4Ge_2$ is a new representative of the $YNiAl_4Ge_2$ structure type. The distances within and between the triangle-mesh layers correspond approximately to a b.c.c. arrangement and the coordination polyhedron around the Ni atoms in the central layer is a slightly deformed cube, shown in Fig. 4. The cube can alternatively be described as a puckered Al-hexagon (similar to cyclohexane in chair conformation) with an additional Al atom above and below the equatorial plane containing the Ni atom (Fig. 5). These hexagons are large enough to store the relatively small Ni atoms, as stated in [2]; the shortest interatomic distances between Al atoms in $ErNiAl_4Ge_2$ are 2.757 Å (2.746 Å in $YNiAl_4Ge_2$).

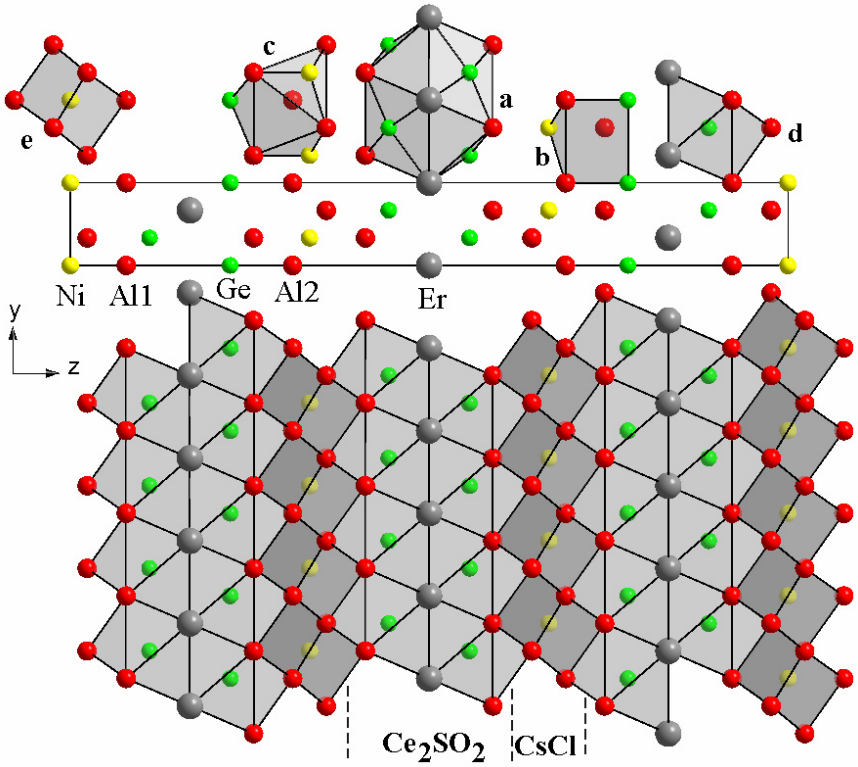


**Fig. 4.** Projection of the unit cell of $ErNiAl_4Ge_2$ on the (100) plane, the coordination polyhedra around Er (a – [**Er**$Ge_6Al_6Er_6$]), Al (b – [**Al1**$NiGe_3Al_3$], c – [**Al2**$Ni_3GeAl_6$]), Ge (d – [**Ge**$Al_4Er_3$]), Ni (e – [**Ni**$Al_8$]), and packing of monocapped octahedra [**Ge**$Al_4Er_3$] and slightly deformed [**Ni**$Al_8$] cubes.

**Table 5** Interatomic distances ($\delta$) and coordination numbers (CN) for $Er_2CoAl_4Ge_2$ (single-crystal diffraction) and $ErNiAl_4Ge_2$ (powder diffraction).

| $Er_2CoAl_4Ge_2$ | | | | $ErNiAl_4Ge_2$ | | | |
|---|---|---|---|---|---|---|---|
| Atoms | | $\delta$(Å) | CN | Atoms | | $\delta$(Å) | CN |
| Er | – 1Ge | 2.912(3) | 18 | Er | – 6Ge | 2.9166(11) | 18 |
| | – 4Ge | 2.9225(6) | | | – 6Al1 | 3.599(4) | |
| | – 4Al | 3.071(4) | | | – 6Er | 4.07160(8) | |
| | – 1Co | 3.572(2) | | Ni | – 2Al1 | 2.392(6) | 8 |
| | – 4Er | 3.844(2) | | | – 6Al2 | 2.4587(14) | |
| | – 4Er | 4.0970(6) | | Al1 | – 1Ni | 2.392(6) | 7 |
| Co | – 8Al | 2.418(2) | 8 | | – 3Ge | 2.554(2) | |
| | [– 2Er | 3.572(2)] | | | – 3Al2 | 2.884(4) | |
| Al | – 2Co | 2.418(2) | 11 | | [– 3Er | 3.599(4)] | |
| | – 1Al | 2.569(5) | | Al2 | – 3Ni | 2.4587(14) | 7 (10) |
| | – 2Ge | 2.796(3) | | | – 1Ge | 2.670(5) | |
| | – 4Al | 2.8970(4) | | | – 3Al2 | 2.757(4) | |
| | – 2Er | 3.071(4) | | | – 3Al1 | 2.884(4) | |
| Ge | – 4Al | 2.796(3) | 9 | Ge | – 3Al1 | 2.554(2) | 7 |
| | – 1Er | 2.912(3) | | | – 1Al2 | 2.670(5) | |
| | – 4Er | 2.9225(6) | | | – 3Er | 2.9166(11) | |

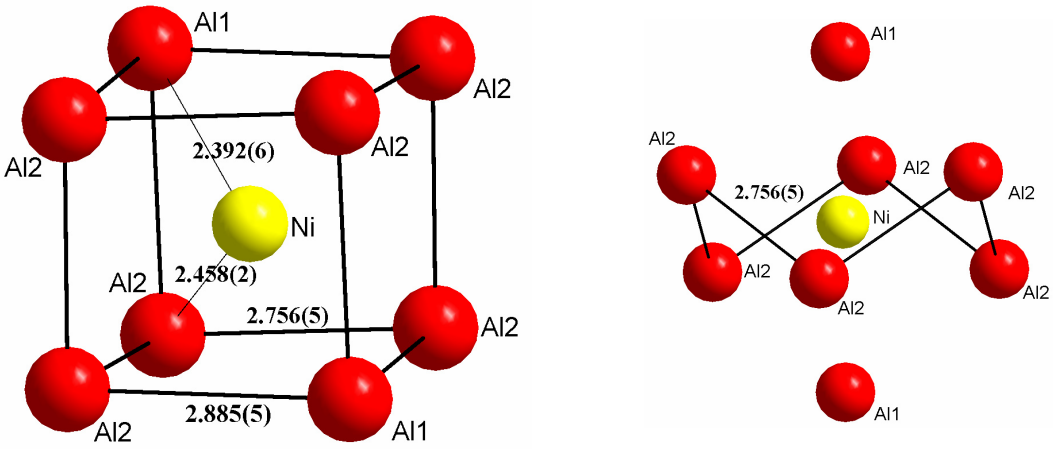


**Fig. 5.** Environment of the Ni atoms in the structure of $ErNiAl_4Ge_2$: presentation as a deformed cube (left) and Al2 atoms in cyclohexane chair conformation (right).

The environment of the Ge atoms consists of three Al atoms at 2.554 Å and one Al atom at 2.670 Å, and can be considered as umbrella-like type coordination. But it is logic to include also the three Er atoms situated at 2.9166 Å in the coordination sphere. The complete coordination polyhedron of the Ge atoms can be described as an octahedron, formed by [$Al_3$] and [$Er_3$] triangles, with one additional Al atom above the [$Al_3$] triangle, which is situated closer to the central atom than the atoms of the [$Er_3$] triangle. Thus, the structure of the $ErNiAl_4Ge_2$ compound belongs to class #11 (coordination number 6÷8 for the smaller atoms) [12]. The coordination polyhedron of the Er atoms is a cubooctahedron formed by an [$Er_6$] hexagon around the central Er atom, two [$Al_3$] triangles situated on each side of this hexagon, and six Ge atoms capping the [$Er_2Al_2$] square faces. The distances between the central atom and the Ge atoms are 2.9166 Å, *i.e.* considerably shorter than the Er-Al distances (3.599 Å). For the site Al1 the coordination polyhedron is a monocapped trigonal prism: three Ge at 2.554 Å and three Al at 2.884 Å form triangles and a Ni atom at 2.392 Å caps the [$Al_3$] face. The coordination polyhedron of the site Al2 is a tricapped tetrahedron formed by three Ni at 2.4587 Å, one Ge at 2.670 Å and three Al at 2.757 Å. Three additional Al atoms at 2.884 Å may also be included in the coordination sphere to form an octahedron with the

other Al atoms around the central Al atom. The complete structure can be described as an intergrowth of slabs formed by [**Ge**$Al_4Er_3$] monocapped octahedra and slabs of slightly deformed [**Ni**$Al_8$] cubes. The former are also found in $ErAl_2Ge_2$ ($Ce_2SO_2$ type) [16], whereas layers similar to the latter are found perpendicular to the body diagonal in NiAl (CsCl type).

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