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# The alumosilicide $HoAl_{2.8}Si_{0.2}$

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**The holmium alumosilicide $HoAl_{2.8}Si_{0.2}$ was synthesized by arc melting and subsequent annealing at 600°C. Its crystal structure was studied by X-ray powder diffraction and identified as $BaPb_3$ type: Pearson symbol *hR*36, space group *R*-3*m*, *a* = 6.12537(7), *c* = 20.9526(3) Å. The structure is close-packed and consists of one-atom thick close-packed layers of composition $Ho(Al,Si)_3$ in $h_2c$ stacking, with 9 layers in the translation period along [001]. The coordination polyhedra are cuboctahedra (sites Ho2 and *M*2) and anticuboctahedra (sites Ho1 and *M*1). For the Ho atoms the coordination polyhedra are built up exclusively of Al/Si atoms, whereas for the latter the composition of the polyhedra is $Ho_4M_8$.**

**Holmium / Aluminum / Silicon / X-ray powder diffraction / Close-packed structure**

## 1. Introduction

With the exception of Eu–Al, the *R*–Al systems, where *R* is a rare-earth metal, are characterized by the formation of binary compounds $RAl_3$ [1,2]. As can be seen from Table 1, the compounds with light rare earths form only one modification and their crystal structure belongs to the hexagonal $Mg_3Cd$ type [3]. The aluminides with heavy rare earths form from one to three different modifications at room temperature (rt), high temperature (ht), and/or high pressure (hp). The crystal structures are all close-packed but belong to four different structure types: cubic $Cu_3Au$ [4], hexagonal $TiNi_3$ [5], trigonal $BaPb_3$ [6], and trigonal $HoAl_3$ [7].

A representative of the structure type $BaPb_3$ has also been reported in the ternary system Ho–Al–Ge (compound $HoAl_{2.8}Ge_{0.2}$ [8]), whereas ternary compounds with the ratio $R$:(Al+{Si,Ge}) ≈ 1:3 in the systems Er–Al–Si and Yb–Al–{Si,Ge} were found to adopt a slightly modified variant of the hexagonal $PuAl_3$ type [9] (compounds $Er_{0.97}Al_{2.8}Si_{0.2}$ [10], $Yb_{0.975}Al_{2.8}Si_{0.2}$ [11], and $Yb_{0.965}Al_{2.8}Ge_{0.2}$ [11]).

In this work we present the results of a structural investigation of the ternary alumosilicide $HoAl_{2.8}Si_{0.2}$. The existence of several ternary compounds has been reported in the Ho–Al–Si system [2,12-14] (Table 2). The compositions of the compounds reported as ~$HoAl_2Si$ (M phase) and ~$Ho_{35}Al_{30}Si_{35}$ (K phase) were later corrected to $Ho_2Al_3Si_2$ and HoAlSi, respectively, whereas ~$Ho_{37.5}Al_{32.5}Si_{30}$ (T phase) may represent the compound $Ho_2Al_2Si$. The compound studied in this work corresponds to the so-called N phase (~$Ho_5Al_{14}Si$) found in [12].

## 2. Experimental

Alloys with a total mass of 1 g were synthesized from high-purity metals (Ho ≥ 99.83, Al ≥ 99.998, and Si ≥ 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 600°C under vacuum in quartz ampoules for 1 month and subsequently quenched in cold water.

Phase and structural analyses were performed based on X-ray powder diffraction data collected on a diffractometer STOE STADI P (Cu $K\alpha_1$ radiation, wavelength $\lambda = 1.5406$ Å) in the angular range $6 \leq 2\theta \leq 110.625°$ with a step of 0.015° and scan time 375 s. The structure was refined by the Rietveld method, using the program DBWS-9807 [21]. Structure drawings were made with the program ATOMS [22].

## 3. Results and discussion

The X-ray diffraction phase analysis showed that the alloy $Ho_{25}Al_{70}Si_5$ was single-phase, whereas the alloys of neighboring compositions were found to contain at least two phases. The crystal structure of the new intermetallide $HoAl_{3-x}Si_x$ ($x = 0.2$), belongs to the rhombohedral structure type $BaPb_3$. In the prototype, the Pb atoms occupy two sites. During the refinement of the structure of the alumosilicide no attempt

**Table 1** Structure types of binary $RAl_3$ and ternary $RAl_{3-x}Si_x$ and $RAl_{3-x}Ge_x$ compounds [1,14].

| Structure type | Pearson symbol | Space group | Sc | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Binary aluminides** | | | | | | | | | | | | | | | | | | |
| $Cu_3Au$ | *cP*4 | *Pm*-3*m* | rt | ht2 | | | | | | | | | hp-ht | ht | ht | rt | rt | rt |
| $Mg_3Cd$ | *hP*8 | $P6_3/mmc$ | | rt | rt | rt | rt | rt | rt | | rt | | | | | | | |
| $BaPb_3$ | *hR*36 | *R*-3*m* | | ht1 | | | | | | | hp-ht | rt | | | | | | |
| $TiNi_3$ | *hP*16 | $P6_3/mmc$ | | | | | | | | | | | rt | hp | | | | |
| $HoAl_3$ | *hR*60 | *R*-3*m* | | | | | | | | | | ht | ht | rt | rt | | | |
| **Ternary alumosilicides** | | | | | | | | | | | | | | | | | | |
| $PuAl_3$ | *hP*24 | $P6_3/mmc$ | | | | | | | | | | | | | rt[a] | | rt[b] | |
| $BaPb_3$ | *hR*36 | *R*-3*m* | | | | | | | | | | | | rt[c] | | | | |
| **Ternary alumogermanides** | | | | | | | | | | | | | | | | | | |
| $PuAl_3$ | *hP*24 | $P6_3/mmc$ | | | | | | | | | | | | | | | rt[d] | |
| $BaPb_3$ | *hR*36 | *R*-3*m* | | | | | | | | | | | | rt[e] | | | | |

[a] Compound $Er(Al_{2.8}Si_{0.2})$.
[b] Partly ordered ternary variant $Yb_{0.975}(Al_{0.985}Si_{0.015})_2(Al_{0.83}Si_{0.17})$ (structure type $Yb_{0.98}Al_{2.8}Si_{0.2}$).
[c] This work.
[d] Partly ordered ternary variant $Yb_{0.965}(Al_{0.985}Ge_{0.015})_2(Al_{0.83}Ge_{0.17})$ (structure type $Yb_{0.98}Al_{2.8}Si_{0.2}$).
[e] Partly ordered ternary variant $HoAl(Al_{0.89}Ge_{0.11})_2$ (structure type $HoAl_{2.8}Ge_{0.2}$).

**Table 2** Crystallographic parameters of compounds reported in the Ho–Al–Si system.

| Compound | Structure type | Pearson symbol | Space group | *a*, Å | *b*, Å | *c*, Å | Reference |
|---|---|---|---|---|---|---|---|
| $HoAl_2Si_2$ | $CaAl_2Si_2$ | *hP*5 | *P*-3*m*1 | 4.19 | – | 6.49 | [15] |
| $\sim HoAl_2Si$ | ... | ... | ... | ... | ... | ... | [12] |
| $\sim Ho_5Al_{14}Si$ | ... | *hR** | ... | 6.117 | – | 20.979 | [12] |
| $HoAl_{2.8}Si_{0.2}$ | $BaPb_3$ | *hR*36 | *R*-3*m* | 6.12537(7) | – | 20.9526(3) | This work |
| $Ho_2Al_3Si_2$ | $Y_2Al_3Si_2$ | *mS*14 | *C*2/*m* | 10.126 | 4.0266<br>$\beta = 100.93°$ | 6.5812 | [16] |
| HoAlSi | YAlGe | *oS*12 | *Cmcm* | 3.9880 | 10.229 | 5.6829 | [17] |
| $\sim Ho_{35}Al_{30}Si_{35}$ | ... | *t*** | ... | 12.123 | – | 15.138 | [12] |
| $\sim Ho_{37.5}Al_{32.5}Si_{30}$ | ... | *t*** | ... | 7.900 | – | 4.255 | [12] |
| $Ho_2AlSi_2$ | $W_2CoB_2$ | *oI*10 | *Immm* | 4.022 | 5.732 | 8.578 | [18] |
| $Ho_2Al_2Si$ | $Mo_2FeB_2$ | *tP*10 | *P*4/*mbm* | 6.910 | – | 4.237 | [19] |
| $Ho_6Al_3Si$ | $Tb_6Al_3Si$ | *tI*80 | *I*4/*mcm* | 11.49 | – | 14.90 | [20] |

was made to distinguish Al and Si and both sites were assumed to be occupied by a statistical mixture of Al and Si atoms. The composition of the statistical mixture (0.93Al + 0.07Si) was calculated according to the nominal composition of the alloy, and the chemical formula is conveniently written as $HoAl_{2.8}Si_{0.2}$. There was no indication for site splitting or vacancies on the *R*-atom sites, as reported for the $Yb_{0.98}Al_{2.8}Si_{0.2}$-type compounds [10,11].

In the final cycle of the refinement, 17 parameters were allowed to vary: zero shift, scale factor, two cell parameters, five profile parameters (pseudo-Voigt function), one texture parameter, three positional parameters, and four displacement parameters.

Experimental details of the structure refinement of the compound $HoAl_{2.8}Si_{0.2}$ and crystallographic data are presented in Table 3. The atom coordinates and isotropic displacement parameters are listed in Table 4, and interatomic distances and atom polyhedra are given in Table 5. Observed and calculated diffraction diagrams are shown in Fig. 1.

In the structure of $HoAl_{2.8}Si_{0.2}$ the Ho atoms occupy two Wyckoff positions, 6*c* and 3*a*, of space group *R*-3*m*. The statistical mixture formed by the smaller atoms (Al and Si) also occupies two Wyckoff positions, however of lower point symmetry, 18*h* and 9*e*.

The crystal structure of the new compound is close-packed with one-atom thick close-packed layers in $h_2c$ stacking along [001] and 9 layers in the translation period **c** (see Fig. 2). The ratio of Ho to Al/Si atoms in each layer is 1:3, and all the layers have the same construction: the Al/Si atoms form kagomé nets 3636 and the Ho atoms center the hexagons in the nets (Fig. 3). The layers are stacked in such a way that the Ho atoms are situated “over” and “under” Al/Si triangles of neighboring nets.

**Table 3** Details of the structure refinement for $HoAl_{2.8}Si_{0.2}$.

| | |
|---|---|
| Space group | $R$-3$m$ |
| Cell parameters $a$, $c$, Å | 6.12537(7), 20.9526(3) |
| Cell volume $V$, Å$^3$ | 680.82(1) |
| Number of formula units in the cell $Z$ | 9 |
| Density $D_X$, g cm$^{-3}$ | 5.399 |
| FWHM parameters $U$, $V$, $W$ | 0.125(4), -0.002(3), 0.0137(5) |
| Mixing parameter $\eta$ | 0.783(4) |
| Asymmetry parameter $C_M$ | -0.013(2) |
| Texture parameter $G$ [direction] | 1.100(1) [001] |
| Number of reflections | 144 |
| Number of refined parameters | 17 |
| Reliability factors $R_B$, $R_p$, $R_{wp}$ | 0.0402, 0.0434, 0.0588 |
| Goodness of fit $S$ | 0.85 |

**Table 4** Atom coordinates and isotropic displacement parameters for $HoAl_{2.8}Si_{0.2}$: structure type $BaPb_3$, $hR36$, $R$-3$m$, $a$ = 6.12537(7), $c$ = 20.9526(3) Å.

| Site | Wyckoff position | $x$ | $y$ | $z$ | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|---|
| Ho1 | 6$c$ | 0 | 0 | 0.2177(1) | 0.62(1) |
| Ho2 | 3$a$ | 0 | 0 | 0 | 0.65(1) |
| $M1$[a] | 18$h$ | 0.4805(1) | 0.5195(1) | 0.2229(1) | 0.59(3) |
| $M2$[a] | 9$e$ | ½ | 0 | 0 | 0.51(4) |

[a] $M1 = M2 = Al_{0.93}Si_{0.07}$.

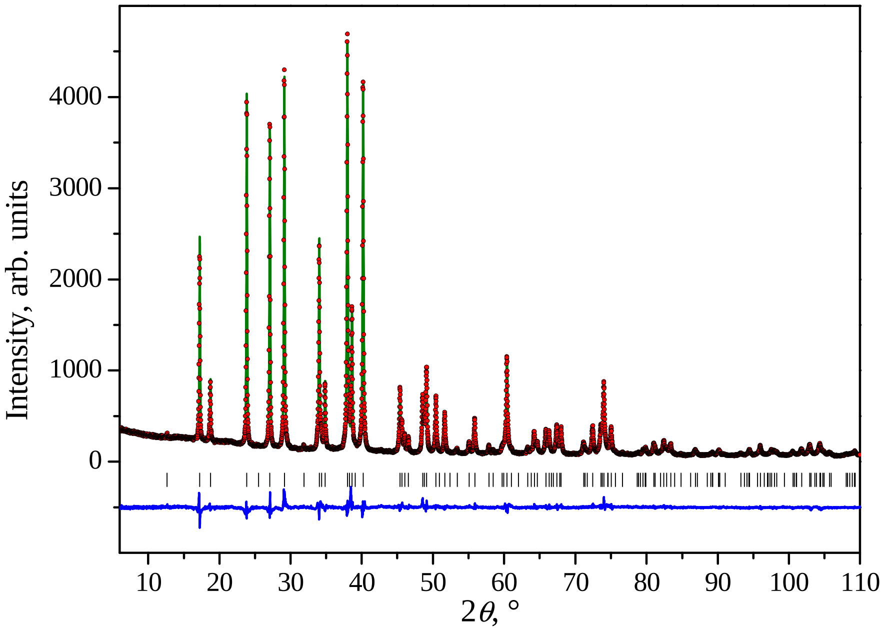
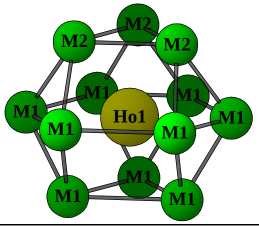
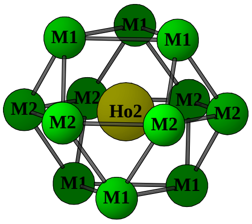
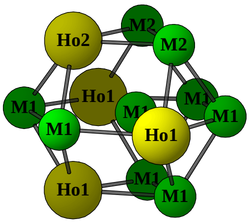
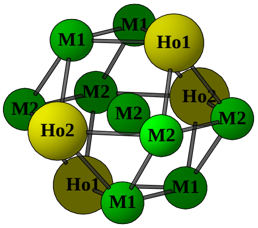


**Fig. 1** Observed (dots), calculated (line) and difference (bottom) X-ray powder diffraction patterns (Cu $K\alpha_1$ radiation) for the sample $Ho_{25}Al_{70}Si_5$ (vertical bars indicate peak positions of the compound $HoAl_{2.8}Si_{0.2}$).

As characteristic of close-packed structures, the coordination polyhedra consist of 12 atoms: cuboctahedra (sites Ho2 and $M2$) and anticuboctahedra (sites Ho1 and $M1$). For the Ho atoms the coordination polyhedra are built up exclusively from Al/Si atoms, whereas for the atoms of the statistical mixture, the composition of the polyhedra is $Ho_4M_8$. In the isotypic compound with Ge, $HoAl_{2.8}Ge_{0.2}$, Ge was found to substitute for Al exclusively on the anticuboctahedral site (Wyckoff position 18$h$) [8].

Cell parameters of the isotypic compounds found in the binary {Y,Gd,Tb}–Al and ternary Ho–Al–{Si,Ge} systems are listed in Table 6. The largest values are observed for the binary compound $GdAl_3$ and

**Table 5** Interatomic distances and coordination polyhedra for $HoAl_{2.8}Si_{0.2}$.

| Atoms | | $\delta$, Å | Polyhedron |
|---|---|---|---|
| Ho1 | -3 $M1^a$<br>-3 $M2^a$<br>-6 $M1^a$ | 2.992(2)<br>2.999(2)<br>3.072(1) |  |
| Ho2 | -6 $M1^a$<br>-6 $M2^a$ | 3.042(2)<br>3.063(1) |  |
| $M1^a$ | 2 $M1^a$<br>2 $M1^a$<br>2 $M2^a$<br>1 Ho1<br>1 Ho2<br>2 Ho1<br>2 $M1^a$ | 2.704(1)<br>2.827(3)<br>2.856(2)<br>2.992(2)<br>3.042(2)<br>3.072(1)<br>3.421(1) |  |
| $M2^a$ | -4 $M1^a$<br>-2 Ho1<br>-2 Ho2<br>-4 $M2^a$ | 2.856(2)<br>2.999(2)<br>3.063(1)<br>3.063(1) |  |

[a] $M1 = M2 = Al_{0.93}Si_{0.07}$.

**Table 6** Cell parameters of compounds with $BaPb_3$-type structure in the systems {Y,Gd,Tb}–Al and Ho–Al–{Si,Ge}.

| Compound | *a*, Å | *c*, Å | *V*, $Å^3$ | Reference |
|---|---|---|---|---|
| $YAl_3$ | 6.195 | 21.137 | 702.52 | [23] |
| $GdAl_3$ | 6.231 | 21.173 | 711.92 | [24] |
| $TbAl_3$ | 6.176 | 21.165 | 699.14 | [25] |
| $HoAl_{2.8}Si_{0.2}$ | 6.12537(7) | 20.9526(3) | 680.82(1) | This work |
| $HoAl_{2.8}Ge_{0.2}$ | 6.1579 | 21.062 | 691.7 | [8] |

the smallest values for the ternary silicon-containing title compound. Within the row of isotypic aluminides the cell parameters decrease with decreasing atomic radius of the rare-earth metal from Gd to Y and Tb ($r_{Gd}$ = 1.802 Å, $r_Y$ = 1.801 Å, $r_{Tb}$ = 1.782 Å [26]). The cell parameters of the alumisilicide are smaller than those of the alumogermanide because of the smaller atomic radii of Si with respect to Ge ($r_{Ho}$ = 1.766 Å, $r_{Si}$ = 1.319 Å, $r_{Ge}$ = 1.369 Å [26]).

Three modifications are known for the binary compound $HoAl_3$ and small additions of Si or Ge produce ternary compounds with a fourth structure. It can be seen from Table 7 that addition of the third component (Si/Ge) or application of high pressure, increases the degree of hexagonality of the close-packing. The structure of the room-temperature modification of the binary compound $HoAl_3$ (own structure type) is characterized by 40% hexagonality, whereas addition of 5 at.% Si leads to the formation of the title compound where the hexagonality is increased to 66.7% (structure type $BaPb_3$). The structure of the high-pressure modification of $HoAl_3$ (structure type $TiNi_3$) has 50% hexagonality. On the contrary, heating to high temperature decreases the hexagonality of the crystal structure down to 0% (structure type $Cu_3Au$). A similar trend is also observed for the binary gallide $HoGa_3$, for which five polymorphic modifications are known [1].

**Table 7** Close-packed structure types with hexagonal $AB_3$-1-type layers [14,27].

| Structure type | Pearson symbol | Space group | Stacking notation | | Hexagonality, % |
|---|---|---|---|---|---|
| | | | Jagodzinski | Zhdanov | |
| $Mg_3Cd$ | $hP8$ | $P6_3/mmc$ | $h$ | $(1)\vert$ | 100 |
| $Ba_{13}Sn_{30}(Sn_{0.36}Bi_{0.64})_9$[a] | $hR156$ | $R$-$3m$ | $h_4ch_3ch_3c$ | $(2)\underline{1}1\underline{2}1(\underline{1})1\underline{2}1\underline{1}$ | 76.9 |
| $Ba_4Sn_9(Sn_{0.42}Bi_{0.58})_3$[a] | $hP32$ | $P6_3/mmc$ | $h_3c$ | $(2)\underline{1}\vert 1$ | 75 |
| $Ba(Tl_{0.2}Pb_{0.8})_3$ | $hP56$ | $P6_3/mmc$ | $h_3ch_2c$ | $2(\underline{1})2\underline{1}\vert 1$ | 71.4 |
| $BaPb_3$[b] | $hR36$ | $R$-$3m$ | $h_2c$ | $(2)(\underline{1})$ | 66.7 |
| $Ta(Rh_{0.33}Pd_{0.67})_3$ | $hP40$ | $P6_3/mmc$ | $h_2chc$ | $2\vert\underline{2}(1)$ | 60 |
| $Ba_5Sn_9(Sn_{0.39}Bi_{0.61})_6$[a] | $hP40$ | $P6_3/mmc$ | $h_3c_2$ | $(3)\underline{1}\vert 1$ | 60 |
| $TiNi_3$ | $hP16$ | $P6_3/mmc$ | $hc$ | $(2)\vert$ | 50 |
| $Mg_3In$[c] | $hR48$ | $R$-$3m$ | $h_2c_2$ | $(3)(\underline{1})$ | 50 |
| $HoAl_3$ | $hR60$ | $R$-$3m$ | $hc_2hc$ | $(3)(\underline{2})$ | 40 |
| $PuAl_3$[d] | $hP24$ | $P6_3/mmc$ | $hc_2$ | $(3)\vert$ | 33.3 |
| $TbGa_2(Ga_{0.64}Sn_{0.36})$[a] [28] | $hR72$ | $R3m$ | $h_2c_4$ | $5\underline{1}$ | 33.3 |
| $Ti(Ni_{0.11}Pt_{0.89})_3$ | $hP28$ | $P$-$3m1$ | $hc_4hc$ | $(5)(\underline{2})$ | 28.6 |
| $Ca_5In_3(In_{0.5}Sn_{0.5})_{12}$[a] [29] | $hP40$ | $P6_3/mmc$ | $hc_4$ | $(5)\vert$ | 20 |
| $Cu_3Au$ | $cP4$ | $Pm$-$3m$ | $c$ | $\infty$ | 0 |

[a] Partly ordered ternary structure.

[b] A partly ordered ternary variant is $HoAl(Al_{0.89}Ge_{0.11})_2$.

[c] A partly ordered ternary variant is $Ba_2Sn_3(Sn_{0.34}Bi_{0.66})_3$.

[d] A partly ordered ternary variant is $Yb_{0.975}(Al_{0.985}Si_{0.015})_2(Al_{0.83}Si_{0.17})$.

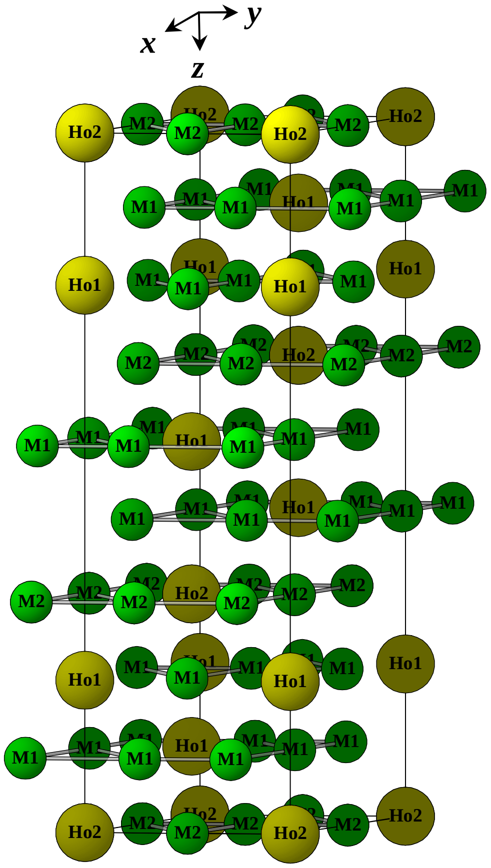


**Fig. 2** Unit cell of the structure of $HoAl_{2.8}Si_{0.2}$. The close-packed layers perpendicular to [001] are emphasized.

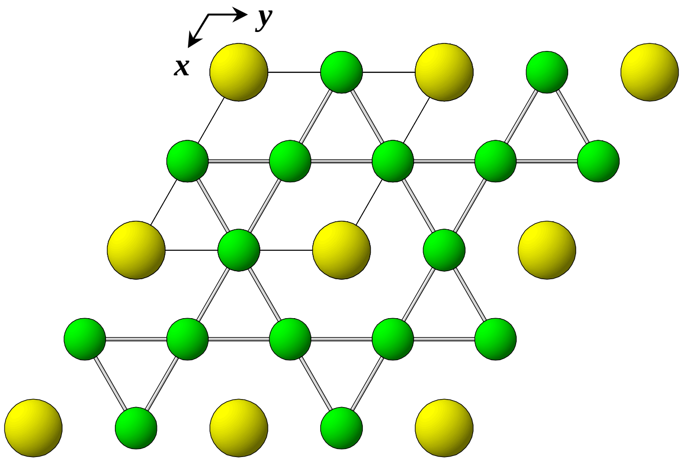


**Fig. 3** Close-packed layer in the structure of $HoAl_{2.8}Si_{0.2}$ ($AB_3$-1-type according to [27]).

## Conclusions

Replacement of 5 at.% Al by Si in $HoAl_3$ at 600ºC changes the structure from close-packed with $hc_2hc$ stacking (own, $HoAl_3$, type) to close-packed with $h_2c$ stacking ($BaPb_3$ type). A similar structure change has earlier been reported for substitution by Ge.

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