

## On the crystal chemistry of new ternary rare earth gold aluminides

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**Eight new rare earth gold aluminides  $R_3Au_xAl_{11-x}$  ( $R = Y, Gd, Ho, Er,$  and  $Tm$ ),  $RAuAl_3$  ( $R = Yb$  and  $Gd$ ) and  $RAu_3Al_7$  ( $R = Y$ ) have been synthesized by arc-melting, followed by annealing at 600°C. The crystal structures of the compounds were solved from powder X-ray diffraction data. The above mentioned intermetallics crystallize with four known structure types,  $La_3Al_{11}$ ,  $BaAl_4$ ,  $BaNiSn_3$ , and  $ScRh_3Si_7$ . Structural peculiarities, coordinations and interactions of the atoms in the investigated compounds are briefly discussed.**

Rare earth intermetallics / Ternary aluminides / X-ray diffraction / Crystal structure

### Introduction

Rare earth – transition metal – aluminium systems have been intensively investigated in recent years [1] with respect to their phase relations, crystal structures and widely varying magnetic and transport properties. Among them, the  $R$ – $Au$ – $Al$  systems have been poorly studied; only the existence of a certain number of isostructural ternary compounds has been reported [2–9]. Investigations of ternary  $Gd_2Au_xAl_{11-x}$  phases with the  $Co_2Si$  structure type (space group  $Pnma$ ) were performed in [2]. The crystal structures (of the  $TiNiSi$  type, space group  $Pnma$ ) and physical properties of equiatomic  $RAuAl$  ( $R = La, Ce$  and  $Nd$ ) aluminides were published in [3]. The authors of [4–5] reported the existence of  $RAu_{2-x}Al_{2+x}$  phases ( $x \sim 0-1$ ) ( $R = La-Yb$ ) with the tetragonal  $BaAl_4$  (space group  $I4/mmm$ ),  $CaBe_2Ge_2$  (space group  $P4/nmm$ ) and  $BaNiSn_3$  (space group  $I4mm$ ) structure types. Examples of novel  $R_3Au_2Al_9$  compounds ( $R = Tb$  and  $Dy$ ) with the orthorhombic  $La_3Al_{11}$  structure type (space group  $Immm$ ) can be found in [8]. New representatives of the  $ScRh_3Si_7$  structure type (space group  $R-3c$ ) in  $R$ – $Au$ – $Al$  ( $R = Ce-Nd, Sm, Gd-Lu$ ) systems were discovered in [9].

In this work the identification of new ternary  $R_3Au_xAl_{11-x}$  ( $R = Y, Gd, Ho, Er,$  and  $Tm$ ),  $RAuAl_3$  ( $R = Yb$  and  $Gd$ ) and  $RAu_3Al_7$  ( $R = Y$ ) are presented.

### Experimental

Starting materials for the synthesis of the  $R$ – $Au$ – $Al$  alloys were rare earth ingots ( $R > 99.9$  wt.%), gold plate (99.99 wt.%) and aluminium rods (99.999 wt.%). Samples with a total weight of 300 mg were prepared by arc-melting buttons in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere, using  $Ti/Zr$  as a getter. The products were turned over and re-melted at least three times in order to ensure homogeneity. Finally fragments of the ingots were wrapped in tantalum foil and sealed in evacuated quartz tubes. Annealing was performed at 600 °C for two weeks. After that, the samples were quenched by submerging the quartz tubes in cold water.

The polycrystalline products were crushed, powdered in an agate mortar, and examined by X-ray powder diffraction. Phase analysis of the alloys was carried out on X-ray diffraction patterns obtained on a HZG-4a diffractometer (Cu  $K\alpha$  radiation). X-ray structural studies were performed using a PANalytical X'Pert Pro diffractometer (Cu  $K\alpha$  radiation). The scans were taken in the  $\theta/2\theta$  mode with the following parameters:  $2\theta$  region 15–120°; step scan 0.03°; counting time per step 20–30 s. The theoretical powder patterns were calculated with the help of the PowderCell program [10]. The lattice parameters were obtained by least-squares fitting using the Latcon program [11]. The FullProf [12] program was used for

the Rietveld refinements. A pseudo-Voigt profile shape function was used. The background was refined with a polynomial function.

## Results and discussion

During the study of as-cast and annealed Al-rich samples we found eight new ternary compounds, namely,  $R_3Au_xAl_{11-x}$  ( $R = Y, Gd, Ho, Er$  and  $Tm$ ),  $RAuAl_3$  ( $R = Yb$  and  $Gd$ ) and  $RAu_3Al_7$  ( $R = Y$ ), with the  $La_3Al_{11}$ ,  $BaAl_4$ ,  $BaNiSn_3$  and  $ScRh_3Si_7$  structure types, respectively. The crystallographic data and structure refinements of the above cited phases are summarized in **Table 1**. Atomic coordinates, isotropic displacement parameters, interatomic distances and coordination numbers (CN) of the atoms can be found in **Tables 2-4**. As examples, the results of the Rietveld refinements of the annealed  $Ho_{21}Au_{18}Al_{61}$ ,  $Yb_{20}Au_{20}Al_{60}$  and  $Y_9Au_{27}Al_{64}$  alloys are shown in **Fig. 1**.

### The $R_3Au_xAl_{11-x}$ ( $R = Y, Gd, Ho, Er, \text{ and } Tm$ ) phases

The ternary  $R_3Au_xAl_{11-x}$  ( $R = Y, Gd, Ho, Er, \text{ and } Tm$ ) phases crystallize with the orthorhombic  $La_3Al_{11}$  structure type (space group  $Immm$ ), a defect version of the  $BaAl_4$  structure type. Two crystallographically independent rare earth sites ( $R1$  and  $R2$ ) build a body-centred tetragonal sublattice, while the  $M$  (Au and Al) atoms form a three-dimensional polyanionic network (**Fig. 2**). Sites  $M1$  ( $2d$ ) and  $M3$  ( $8l$ ) are occupied by aluminium atoms. About 1/8 Au and 7/8 Al atoms are situated in the  $M2$  ( $4h$ ) site. Site  $M4$  ( $8l$ ) displays an occupation by 1/2 Au and 1/2 Al atoms. The  $R1$  and  $R2$  atoms centre 16-vertex polyhedra [ $M_{16}$ ]. The coordination polyhedra of the  $M1$  and  $M2$  atoms are distorted cubooctahedra [ $R_4M_8$ ], and the surrounding atoms of the  $M3$  and  $M4$  atoms form 10-vertex polyhedra, [ $R_4M_6$ ] and [ $R_5M_5$ ], respectively.

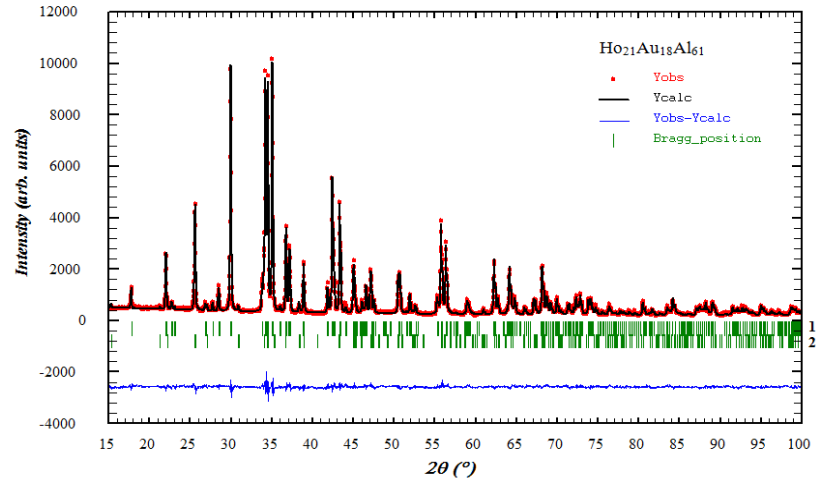
Interatomic distances and coordination numbers of the atoms in  $R_3Au_xAl_{11-x}$  are presented in **Table 3**. The shortest  $R-M$  distances are smaller than the sums of the atomic radii [13],  $r(R) + r(Au, Al)$ , for the following atoms:  $R1-M4$  (3.187-3.253 Å),  $R2-M1$  (3.154-3.169 Å),  $R2-M2$  (3.132-3.192 Å),  $R2-M3$  (3.101-3.173 Å) and  $R2-M4$  (3.133-3.220 Å). The shortest  $M-M$  distances range from 2.475 to 3.061 Å. The  $M1-M3$  (2.824-2.955 Å) and  $M1-M2$  (2.969-3.061 Å) distances are close to the sum of the metallic radii  $r(Au)$  and  $r(Al)$  [13]. Significantly shorter  $M-M$  distances are also observed for the following pairs:  $M2-M3$  (2.769-2.858 Å),  $M2-M4$  (2.475-2.516 Å),  $M3-M4$  (2.520-2.633 Å) and  $M4-M4$  (2.646-2.732 Å). This can indicate partial bonding character between the above cited  $M$  atoms. For comparison, the  $M2-M4$ ,  $M3-M4$  and  $M4-M4$  distances are consistent with twice the covalent radius of Al, which is 1.26 Å.

It should be noted that ternary rare earth aluminides with  $La_3Al_{11}$  structure type have also been found in systems with copper, silver and zinc [14-16]. Moreover, structures related to the  $La_3Al_{11}$ -type [17], such as  $Ho_3Ni_{1.8}Ga_{9.2}$ ,  $Dy_3Co_6Sn_5$ ,  $Yb_3Au_{5.5}Ga_{5.5}$ ,  $Ca_3Au_{7.16}Ge_{3.84}$ ,  $Ca_3Au_8Ge_3$ ,  $La_3Au_4In_7$ , and  $Er_3Pd_7P_4$ , have been identified in other  $R-T-X$  systems [1].

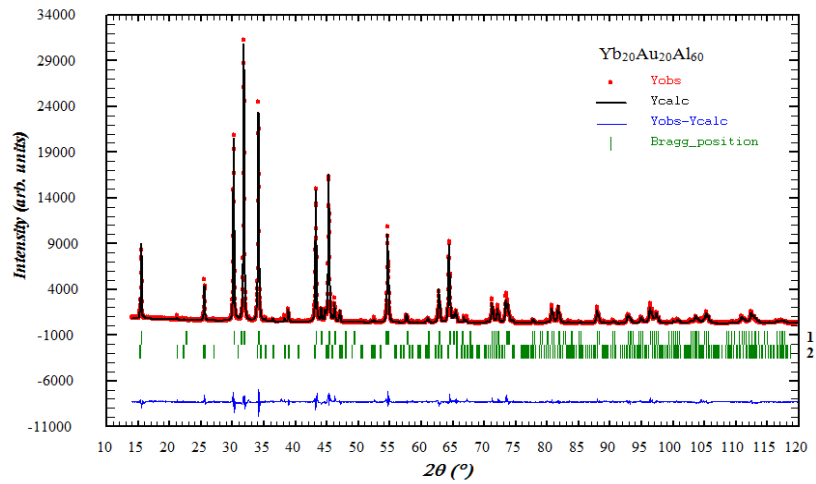
### The $RAuAl_3$ ( $R = Gd \text{ and } Yb$ ) phases

The ternary phase  $YbAuAl_3$  was prepared for the first time. The ytterbium atoms occupy the Ba site of the tetragonal  $BaAl_4$  structure type (space group  $I4/mmm$ ), whereas the atoms of gold and aluminum ( $M$ ) are statistically distributed over the Al sites (see **Table 2**). The values of the interatomic distances are in good agreement with the sums of the atomic radii of the respective components [13]. The shortest  $Yb-M$  and  $M-M$  distances range from 3.226 to 3.533 Å and from 2.576 to 2.957 Å, respectively (**Table 4**). More detailed analyses of the structures of  $RAu_2Al_2$  and  $RAuAl_3$  compounds with  $BaAl_4$ -type can be found in [4,7].

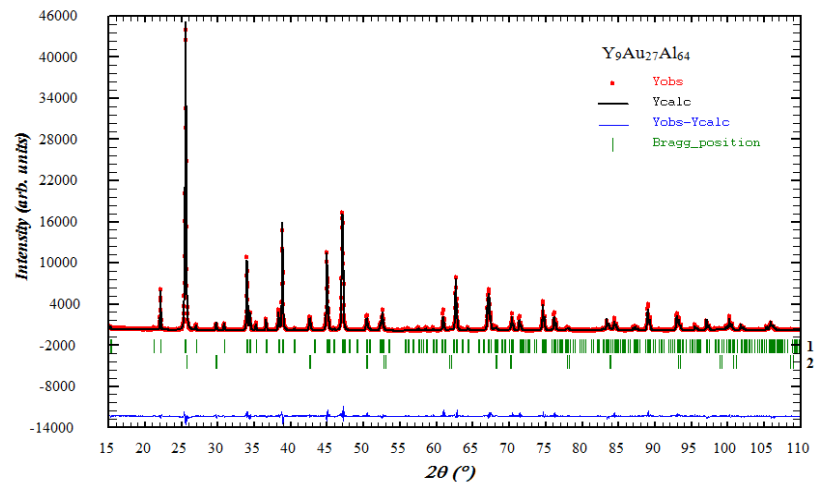
The intermetallic compound with the composition  $GdAuAl_3$  was first reported in [7]. A structure with a partly ordered version of the  $BaAl_4$  structure type was proposed by the authors. However, details of the crystal structure refinement were not presented. Our investigation of the structure of  $GdAuAl_3$  was performed using powder X-ray diffraction data. The structure was first refined in the centrosymmetric space group  $I4/mmm$  ( $BaAl_4$ -type). However, this refinement showed unreasonable results (negative displacement parameters, higher value of the residual factor,  $R_B = 11.1\%$ ). Several additional structural (ordered and disordered) models were tested. Reasonable results (see **Tables 1 and 2**) were obtained in the case of the  $BaNiSn_3$  structure type (space group  $I4mm$ ). The residual factor  $R_B$  was lowered to 4.85%. The Gd atoms occupy the  $2a$  (Ba) site; the  $4b$  (Sn) site and the two other  $2a$  (Ni, Sn) sites revealed mixing of Au and Al atoms. The neighbours of the gadolinium atoms form 16-vertex polyhedra [ $M_{16}$ ]. The coordination polyhedra of the  $M1$  and  $M2$  atoms have the form of tri-capped deformed trigonal prisms [ $Gd_4M_5$ ]. The  $M3$  atoms are located inside distorted cuboctahedra. A projection of the  $GdAuAl_3$  structure onto the  $XZ$  plane and the three-dimensional [ $AuAl_3$ ] network are shown in **Fig. 3**. Interatomic distances in the structure of  $GdAuAl_3$  are listed in **Table 4**. The  $Gd-M$  distances vary within a wide range, however, the by far shortest distances (3.198 Å) are formed between Gd and  $M2$  atoms. The shortest  $M-M$  distances range from 2.524 to 2.608 Å, indicating strong interactions between these atoms.



(a)



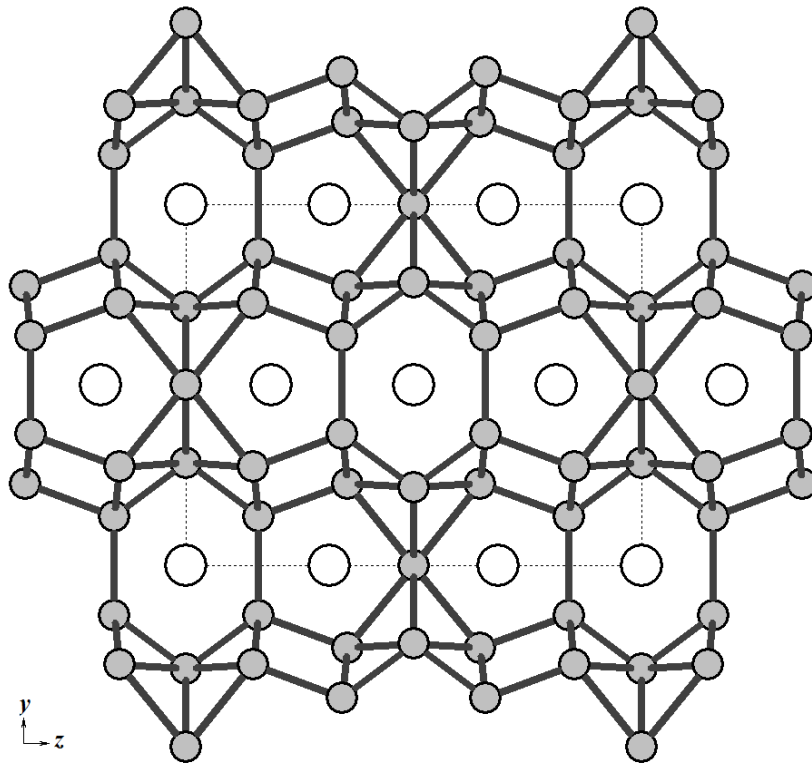
(b)



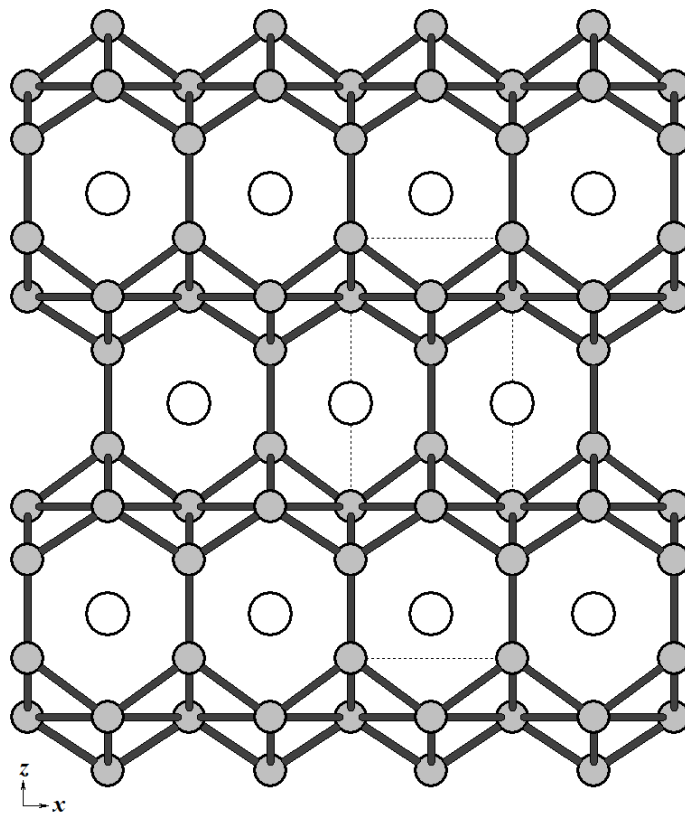
(c)

**Fig. 1** X-ray diffraction patterns of some R–Au–Al alloys:

(a)  $\text{Ho}_{21}\text{Au}_{18}\text{Al}_{61}$  (1 –  $\text{Ho}_3\text{Au}_{2.63}\text{Al}_{8.37}$ ,  $w = 90\%$ ,  $R_B = 4.24\%$ ; 2 –  $\text{HoAu}_3\text{Al}_7$ ,  $w = 10\%$ ,  $R_B = 7.46\%$ ) (Cu  $K\alpha$  radiation,  $R_p = 5.86\%$ ,  $R_{wp} = 7.61\%$ ); (b)  $\text{Yb}_{20}\text{Au}_{20}\text{Al}_{60}$  (1 –  $\text{YbAuAl}_3$ ,  $w = 95\%$ ,  $R_B = 4.03\%$ ; 2 –  $\text{YbAu}_3\text{Al}_7$ ,  $w = 5\%$ ,  $R_B = 14.1\%$ ) (Cu  $K\alpha$  radiation,  $R_p = 6.48\%$ ,  $R_{wp} = 8.30\%$ ); (c)  $\text{Y}_9\text{Au}_{27}\text{Al}_{64}$  (1 –  $\text{YAu}_3\text{Al}_7$ ,  $w = 93\%$ ,  $R_B = 5.62\%$ ; 2 –  $\text{AuAl}_2$ ,  $w = 7\%$ ,  $R_B = 7.28\%$ ) (Cu  $K\alpha$  radiation,  $R_p = 8.44\%$ ,  $R_{wp} = 11.6\%$ ).



**Fig. 2** Projection of the  $R_3Au_xAl_{11-x}$  structure onto the  $YZ$  plane. White circles represent  $R$  atoms and grey filled circles  $M$  (Au and Al) atoms.



**Fig. 3** Projection of the  $GdAuAl_3$  structure onto the  $XZ$  plane. White circles represent Gd atoms and grey filled circles  $M$  (Au and Al) atoms.

**Table 1** Parameters for the data collection and structure refinement of the R–Au–Al compounds.

Phase	$\text{Y}_3\text{Au}_{2.27}\text{Al}_{8.73}$	$\text{Gd}_3\text{Au}_{2.26}\text{Al}_{8.74}$	$\text{Ho}_3\text{Au}_{2.63}\text{Al}_{8.37}$	$\text{Er}_3\text{Au}_{2.43}\text{Al}_{8.57}$
Structure type	$\text{La}_3\text{Al}_{11}$	$\text{La}_3\text{Al}_{11}$	$\text{La}_3\text{Al}_{11}$	$\text{La}_3\text{Al}_{11}$
Space group	<i>Immm</i> (No. 71)	<i>Immm</i> (No. 71)	<i>Immm</i> (No. 71)	<i>Immm</i> (No. 71)
Z	2	2	2	2
Pearson symbol	<i>oI28</i>	<i>oI28</i>	<i>oI28</i>	<i>oI28</i>
Cell parameters				
<i>a</i> (Å)	4.2702(1)	4.2947(1)	4.2576(1)	4.2477(1)
<i>b</i> (Å)	9.9883(2)	9.9991(2)	9.9646(2)	9.9529(3)
<i>c</i> (Å)	12.5674(3)	12.6565(3)	12.5123(3)	12.4725(3)
<i>V</i> (Å <sup>3</sup> )	536.02(2)	543.50(2)	530.84(2)	527.29(2)
Diffractometer	PANalytical	PANalytical	PANalytical	PANalytical
Radiation	CuK $\alpha$	CuK $\alpha$	CuK $\alpha$	CuK $\alpha$
2 $\theta$ range (°)	15-120	15-120	15-100	15-100
Counting step (°)	0.03	0.03	0.03	0.03
Counting time (s)	20	30	20	20
Number of reflections	252	256	178	176
Number of refined parameters	34	33	34	33
Reliability factors				
<i>R</i> <sub>B</sub> (%)	7.86	4.61	4.24	4.87
<i>R</i> <sub>F</sub> (%)	6.11	3.25	3.45	4.19
<i>R</i> <sub>p</sub> (%)	7.52	4.96	5.86	6.53
<i>R</i> <sub>wp</sub> (%)	9.74	6.31	7.61	8.41
$\chi^2$	3.66	3.86	3.42	4.69
Phase	$\text{Tm}_3\text{Au}_{2.07}\text{Al}_{8.93}$	$\text{YbAu}_{0.95}\text{Al}_{3.05}$	$\text{GdAu}_{1.02}\text{Al}_{2.98}$	$\text{YAu}_{3.06}\text{Al}_{6.94}$
Structure type	$\text{La}_3\text{Al}_{11}$	$\text{BaAl}_4$	$\text{BaNiSn}_3$	$\text{ScRh}_3\text{Si}_7$
Space group	<i>Immm</i> (No. 71)	<i>I4/mmm</i> (No. 139)	<i>I4mm</i> (No. 107)	<i>R-3c</i> (No. 167)
Z	2	2	2	6
Pearson symbol	<i>oI28</i>	<i>tI10</i>	<i>tI10</i>	<i>hR66</i>
Cell parameters				
<i>a</i> (Å)	4.2387(1)	4.18225(6)	4.21658(7)	8.0224(1)
<i>b</i> (Å)	9.9539(2)	–	–	–
<i>c</i> (Å)	12.4101(3)	11.3927(2)	10.9760(3)	20.9708(3)
<i>V</i> (Å <sup>3</sup> )	523.60(2)	199.267(6)	195.149(6)	1168.84(3)
Diffractometer	PANalytical	PANalytical	PANalytical	PANalytical
Radiation	Cu K $\alpha$	Cu K $\alpha$	Cu K $\alpha$	Cu K $\alpha$
2 $\theta$ range (°)	15-100	15-120	15-120	15-110
Counting step (°)	0.03	0.03	0.03	0.03
Counting time (s)	20	30	20	25
Number of reflections	176	63	61	168
Number of refined parameters	32	23	26	27
Reliability factors				
<i>R</i> <sub>B</sub> (%)	5.91	4.03	4.85	5.62
<i>R</i> <sub>F</sub> (%)	4.57	3.33	3.46	4.33
<i>R</i> <sub>p</sub> (%)	5.74	6.48	7.09	8.44
<i>R</i> <sub>wp</sub> (%)	7.59	8.30	9.21	11.6
$\chi^2$	4.60	6.27	2.17	8.16

**Table 2** Atomic coordinates and displacement parameters for the structures of the *R*-Au-Al compounds.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )	Occupation (%)
<b>Y<sub>3</sub>Au<sub>2.27</sub>Al<sub>8.73</sub> (space group <i>I</i>mmm)</b>						
<i>R</i> 1	2 <i>a</i>	0	0	0	0.81(12)	100Y
<i>R</i> 2	4 <i>i</i>	0	0	0.3153(2)	0.80(9)	100Y
<i>M</i> 1	2 <i>d</i>	½	0	½	1.0(3)	3.9(4)Au+96.1(4)Al
<i>M</i> 2	4 <i>h</i>	0	0.2193(5)	½	0.88(17)	13.8(3)Au+86.2(3)Al
<i>M</i> 3	8 <i>l</i>	0	0.2770(6)	0.1431(5)	1.02(16)	1.3(2)Au+98.7(2)Al
<i>M</i> 4	8 <i>l</i>	0	0.36753(15)	0.33986(16)	1.12(6)	47.6(4)Au+52.4(4)Al
<b>Gd<sub>3</sub>Au<sub>2.26</sub>Al<sub>8.74</sub> (space group <i>I</i>mmm)</b>						
<i>R</i> 1	2 <i>a</i>	0	0	0	0.61(8)	100Gd
<i>R</i> 2	4 <i>i</i>	0	0	0.31587(14)	0.65(6)	100Gd
<i>M</i> 1	2 <i>d</i>	½	0	½	1.0(3)	100Al
<i>M</i> 2	4 <i>h</i>	0	0.2182(6)	½	1.3(2)	14.4(5)Au+85.6(5)Al
<i>M</i> 3	8 <i>l</i>	0	0.2714(5)	0.1460(5)	1.1(2)	2.4(2)Au+97.6(2)Al
<i>M</i> 4	8 <i>l</i>	0	0.36337(12)	0.33995(14)	1.30(6)	50.5(3)Au+49.5(3)Al
<b>Ho<sub>3</sub>Au<sub>2.63</sub>Al<sub>8.37</sub> (space group <i>I</i>mmm)</b>						
<i>R</i> 1	2 <i>a</i>	0	0	0	0.75(10)	100Ho
<i>R</i> 2	4 <i>i</i>	0	0	0.31292(17)	0.98(8)	100Ho
<i>M</i> 1	2 <i>d</i>	½	0	½	1.0(3)	1.6(4)Au+98.4(4)Al
<i>M</i> 2	4 <i>h</i>	0	0.2157(5)	½	1.02(13)	14.7(3)Au+85.3(3)Al
<i>M</i> 3	8 <i>l</i>	0	0.2728(5)	0.1460(5)	1.04(14)	4.5(2)Au+95.5(2)Al
<i>M</i> 4	8 <i>l</i>	0	0.36387(13)	0.34123(16)	1.02(7)	53.5(3)Au+46.5(3)Al
<b>Er<sub>3</sub>Au<sub>2.43</sub>Al<sub>8.57</sub> (space group <i>I</i>mmm)</b>						
<i>R</i> 1	2 <i>a</i>	0	0	0	0.69(11)	100Er
<i>R</i> 2	4 <i>i</i>	0	0	0.31197(18)	0.77(9)	100Er
<i>M</i> 1	2 <i>d</i>	½	0	½	1.2(4)	100Al
<i>M</i> 2	4 <i>h</i>	0	0.2085(7)	½	1.17(17)	11.8(3)Au+88.2(3)Al
<i>M</i> 3	8 <i>l</i>	0	0.2729(6)	0.1526(8)	1.17(16)	4.0(2)Au+96.0(2)Al
<i>M</i> 4	8 <i>l</i>	0	0.36413(15)	0.3411(2)	1.27(9)	50.7(3)Au+49.3(3)Al
<b>Tm<sub>3</sub>Au<sub>2.07</sub>Al<sub>8.93</sub> (space group <i>I</i>mmm)</b>						
<i>R</i> 1	2 <i>a</i>	0	0	0	0.65(11)	100Tm
<i>R</i> 2	4 <i>i</i>	0	0	0.31103(17)	0.77(9)	100Tm
<i>M</i> 1	2 <i>d</i>	½	0	½	1.4(4)	100Al
<i>M</i> 2	4 <i>h</i>	0	0.2133(6)	½	1.0(2)	17.2(3)Au+82.8(3)Al
<i>M</i> 3	8 <i>l</i>	0	0.2797(7)	0.1434(8)	1.2(2)	100Al
<i>M</i> 4	8 <i>l</i>	0	0.36647(18)	0.3410(3)	0.80(10)	43.2(3)Au+56.8(3)Al
<b>YbAu<sub>0.95</sub>Al<sub>3.05</sub> (space group <i>I</i>4/<i>mmm</i>)</b>						
<i>R</i>	2 <i>a</i>	0	0	0	0.68(4)	100Yb
<i>M</i> 1	4 <i>d</i>	0	½	¼	1.26(5)	6.7(2)Au+93.3(2)Al
<i>M</i> 2	4 <i>e</i>	0	0	0.38695(9)	1.54(14)	46.0(4)Au+54.0(4)Al
<b>GdAu<sub>1.02</sub>Al<sub>2.98</sub> (space group <i>I</i>4<i>mm</i>)</b>						
<i>R</i>	2 <i>a</i>	0	0	0.6055(9)	0.97(8)	100Gd
<i>M</i> 1	2 <i>a</i>	0	0	0.2337(6)	0.96(7)	80.8(8)Au+19.2(8)Al
<i>M</i> 2	2 <i>a</i>	0	0	0	0.98(18)	14.9(6)Au+85.1(6)Al
<i>M</i> 3	4 <i>b</i>	0	½	0.3602(14)	0.96(13)	3.1(3)Au+96.9(3)Al
<b>YAu<sub>3.06</sub>Al<sub>6.94</sub> (space group <i>R</i>-3<i>c</i>)</b>						
<i>R</i>	6 <i>b</i>	0	0	0	1.00(12)	100Y
<i>M</i> 1	6 <i>a</i>	0	0	¼	1.3(6)	100Al
<i>M</i> 2	18 <i>e</i>	0.32503(16)	0	¼	0.98(2)	98.6(1)Au+1.4(1)Al
<i>M</i> 3	36 <i>f</i>	0.0103(10)	0.2072(8)	0.1358(3)	1.17(2)	1.7(1)Au+98.3(1)Al

**Table 3** Interatomic distances ( $d$ ) and coordination numbers (CN) of the atoms in the structures of the  $R_3Au_xAl_{1-x}$  compounds.

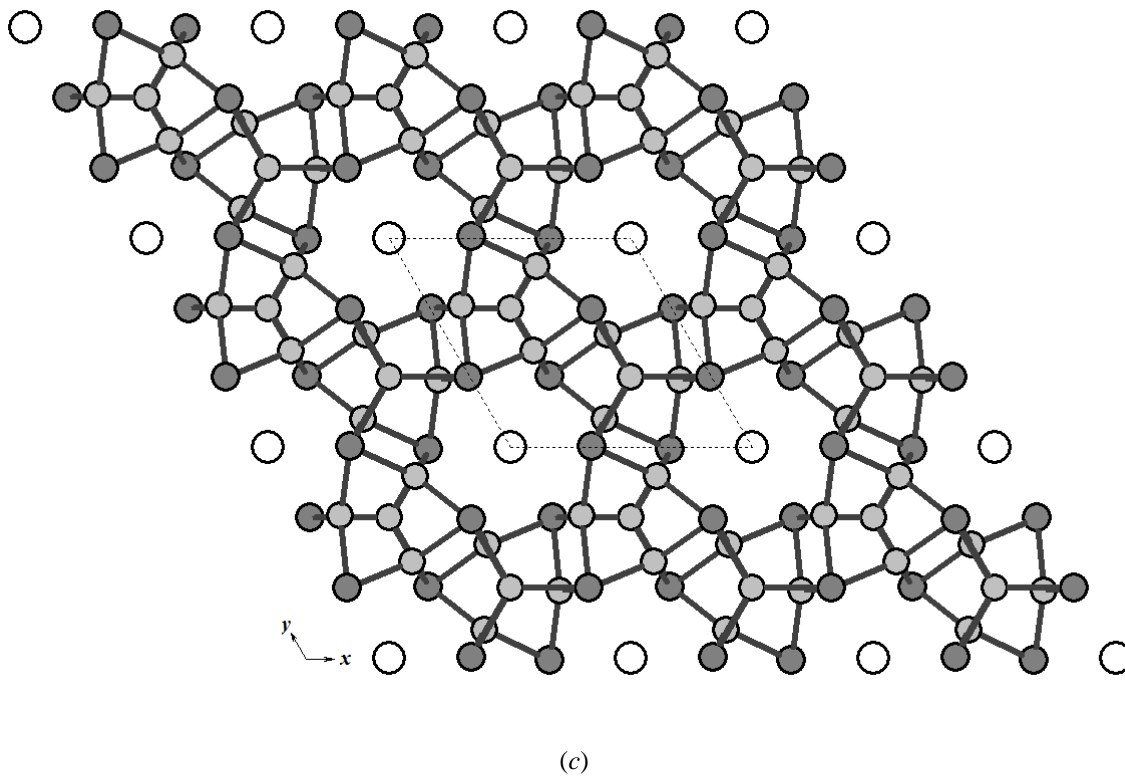
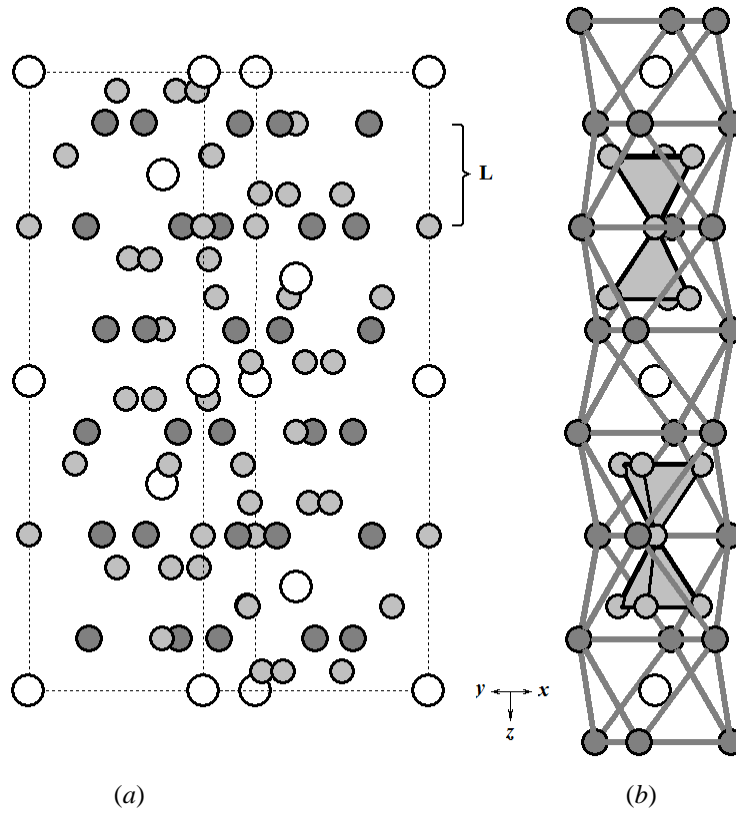
Atoms	$d$ (Å)	$d$ (Å)	$d$ (Å)	$d$ (Å)	$d$ (Å)	CN
$R$	Y	Gd	Ho	Er	Tm	
$R1-8M4$	3.219(1)	3.253(1)	3.212(1)	3.205(2)	3.187(2)	16
$R1-4M3$	3.300(6)	3.283(5)	3.275(5)	3.317(7)	3.305(8)	
$R1-4M2$	3.524(4)	3.543(5)	3.544(4)	3.596(6)	3.555(5)	
$R2-4M3$	3.129(4)	3.173(4)	3.150(4)	3.133(4)	3.101(6)	16
$R2-2M1$	3.154(2)	3.169(1)	3.164(2)	3.164(2)	3.161(2)	
$R2-4M4$	3.180(2)	3.220(2)	3.177(2)	3.159(2)	3.133(2)	
$R2-2M2$	3.192(4)	3.192(4)	3.178(4)	3.132(5)	3.163(4)	
$R2-2M3$	3.513(6)	3.462(6)	3.428(6)	3.366(7)	3.476(9)	
$R2-2M4$	3.684(2)	3.646(1)	3.643(1)	3.642(2)	3.667(2)	
$M1-4M3$	2.862(6)	2.939(6)	2.909(6)	2.955(7)	2.824(9)	
$M1-4M2$	3.059(4)	3.061(4)	3.025(4)	2.969(5)	3.000(4)	
$M1-4R2$	3.154(2)	3.169(1)	3.164(2)	3.164(2)	3.161(2)	
$M2-2M4$	2.499(4)	2.492(4)	2.475(4)	2.516(5)	2.494(5)	12
$M2-4M3$	2.791(4)	2.834(4)	2.807(4)	2.858(6)	2.769(6)	
$M2-2M1$	3.059(4)	3.061(4)	3.025(4)	2.969(5)	3.000(4)	
$M2-2R2$	3.192(4)	3.192(4)	3.178(4)	3.132(5)	3.163(4)	
$M2-2R1$	3.524(4)	3.543(5)	3.544(4)	3.596(6)	3.555(5)	
$M3-2M4$	2.586(3)	2.541(3)	2.532(3)	2.525(3)	2.578(4)	10
$M3-1M4$	2.633(6)	2.622(6)	2.606(7)	2.520(9)	2.599(10)	
$M3-2M2$	2.791(4)	2.834(4)	2.807(4)	2.858(6)	2.769(6)	
$M3-1M1$	2.862(6)	2.939(6)	2.909(6)	2.955(7)	2.824(9)	
$M3-2R2$	3.129(4)	3.173(4)	3.150(4)	3.133(4)	3.101(6)	
$M3-1R1$	3.300(6)	3.283(5)	3.275(5)	3.317(7)	3.305(8)	
$M3-1R2$	3.513(6)	3.462(6)	3.428(6)	3.366(7)	3.476(9)	
$M4-1M2$	2.499(4)	2.492(4)	2.475(4)	2.516(5)	2.494(5)	10
$M4-2M3$	2.586(3)	2.541(3)	2.532(3)	2.525(3)	2.578(4)	
$M4-1M3$	2.633(6)	2.622(6)	2.606(7)	2.520(9)	2.599(10)	
$M4-1M4$	2.646(2)	2.732(2)	2.713(2)	2.705(2)	2.658(3)	
$M4-2R2$	3.180(2)	3.220(2)	3.177(2)	3.159(2)	3.133(2)	
$M4-2R1$	3.219(1)	3.253(1)	3.212(1)	3.205(2)	3.187(2)	
$M4-1R2$	3.684(2)	3.646(1)	3.643(1)	3.642(2)	3.667(2)	

According to [1], there exists a large family of intermetallic rare earth- $d$ -metal- $p$ -metal phases that form with the  $BaAl_4$ -type (or its superstructures). The occupation preferences of the  $d$ - and  $p$ -metals in these phases are complex and depend on the atomic size and the relative electronegativities of the elements. Formation of disordered and/or deformed structures of the  $BaAl_4$ -type are also typical for ternary rare earth based systems. The structures of  $BaGa_2P_2$ ,  $BaMg_2Sn_2$ ,  $BaNi_2Si_2$ ,  $BaNiSn_3$ ,  $BaPt_2Ge_2$ ,  $CaBe_2Ge_2$ ,  $CaCu_{0.15}Ga_{3.85}$ ,  $CaGa_4$ ,  $CeAl_2Ga_2$ ,  $CeCu_{2-x}In_{2-y}$ ,  $CeNi_{2.36}Sb_{1.64}$ ,  $CePtGa_3$ ,  $EuGa_2P_2$ ,  $LaPt_2Ge_2$ ,  $LaPt_{1.42}Pd_{0.58}Ge_2$ ,  $SrMgIn_3$ , and  $URh_{2-x}As_{2-y}$  can be obtained from the  $BaAl_4$  structure type [17].

#### The $RAu_3Al_7$ ( $R = Y$ ) phase

The new intermetallic compound  $YAu_3Al_7$  belongs to the rhombohedral  $ScRh_3Si_7$  structure type (space group  $R-3c$ ). The unit cell and the atomic arrangement in this structure are shown in Fig. 4. The Au atoms (18e site) form a hexagonal close-packed arrangement. The Al atoms (6a and 36f sites) form tetrahedra connected by common vertices to  $[Al_7]$  clusters. Two thirds of the  $[Au_6]$  octahedra connected by common faces are occupied by Al tetrahedra, the remaining octahedral voids are occupied by Y atoms (6b site).

Interatomic distances and the nearest neighbors of the atoms in the  $YAu_3Al_7$  structure are given in Table 4. The Y atoms are located inside 18-vertex



**Fig. 4** Unit cell (a),  $[Au_6]$  octahedra and  $[Al_7]$  clusters (b), and part (L) of the three-dimensional  $[Au_3Al_7]$  network (c) in the structure of  $YAu_3Al_7$ . White circles represent Y atoms, dark grey circles Au atoms, and light grey circles Al atoms.



**Table 4** Interatomic distances ( $d$ ) and coordination numbers (CN) of the atoms in the structures of the  $RAuAl_3$  ( $R = Yb$  and  $Gd$ ) and  $RAu_3Al_7$  ( $R = Y$ ) compounds.

Atoms	$d$ (Å)	CN	Atoms	$d$ (Å)	CN
YbAuAl <sub>3</sub>			YAu <sub>3</sub> Al <sub>7</sub>		
Yb–8M2	3.226(1)	16	Y–6M2	3.223(1)	18
Yb–8M1	3.533(1)		Y–6M3	3.278(6)	
			Y–6M3	3.342(5)	
M1–4M2	2.609(1)	12			
M1–4M1	2.957(1)		M1–3M2	2.608(1)	9
M1–4Yb	3.533(1)		M1–6M3	2.892(6)	
M2–M2	2.576(1)	9	M2–2M3	2.572(6)	9
M2–4M1	2.609(1)		M2–2M3	2.591(6)	
M2–4Yb	3.226(1)		M2–1M1	2.608(1)	
			M2–2M3	2.638(6)	
			M2–2Y	3.223(1)	
GdAuAl <sub>3</sub>					
Gd–4M2	3.198(4)	16	M3–1M2	2.572(6)	10
Gd–4M1	3.297(5)		M3–1M2	2.591(6)	
Gd–4M3	3.420(14)		M3–1M2	2.638(6)	
Gd–4M3	3.502(15)		M3–2M3	2.810(6)	
			M3–1M3	2.814(9)	
M1–4M3	2.524(9)	9	M3–1M3	2.882(11)	
M1–1M2	2.566(7)		M3–1M1	2.892(6)	
M1–4Gd	3.297(5)		M3–1Y	3.278(6)	
			M3–1Y	3.342(5)	
M2–M1	2.566(7)	9			
M2–4M3	2.608(9)				
M2–4Gd	3.198(4)				
M3–2M1	2.524(9)	12			
M3–2M2	2.608(9)				
M3–4M3	2.982(1)				
M3–2Gd	3.420(14)				
M3–2Gd	3.502(15)				

(roughly spherical) polyhedra [Au<sub>6</sub>Al<sub>12</sub>]. The coordination polyhedra of the M1 (Al) atoms are tri-capped deformed trigonal prisms [Au<sub>3</sub>Al<sub>6</sub>]. 9- and 10-vertex polyhedra, namely, [Y<sub>2</sub>Al<sub>7</sub>] and [Y<sub>2</sub>Au<sub>3</sub>Al<sub>15</sub>], are the coordination polyhedra of the M2 (Au) and M3 (Al) atoms, respectively. The Y–M distances are close to the sum of the radii of the Y/Au or Y/Al atoms [13]. Strong interactions are observed between M atoms. The shortest interatomic distances were found to be 2.608 Å (M1–M2), 2.572 Å (M2–M3) and 2.810 Å (M3–M3).

It should be underlined that ternary compounds with layered structures (YNi<sub>3</sub>Al<sub>9</sub>, Y<sub>2</sub>Co<sub>3</sub>Al<sub>9</sub>, Gd<sub>3</sub>Ru<sub>4</sub>Al<sub>12</sub>, etc.), which are similar to the ScRh<sub>3</sub>Si<sub>7</sub> structure type, have been found in many rare earth – transition metal – aluminium systems [1]. The structures of some of these phases have been briefly reviewed in [18,19].

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