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Research Paper

Synthesis, Characterization and X-ray Studies of *RE*AuAl (*RE* = Y, Eu, Lu) Intermetallic Complexes

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ABSTRACT

The intermetallic compounds were synthesized from the elements in sealed tantalum ampoules using high-frequency furnace followed by annealing for crystal growth. They were characterized by powder and single crystal X-ray diffraction. YAuAl and EuAuAl phases crystallize with an orthorhombic TiNiSi type structure, space group Pnma while LuAuAl with smaller size rare earth element adopts a hexagonal ZrNiAl type structure, space group P$\bar{6}$2m. The structure refinements indicate small homogeneity ranges for $YAu_{1\pm x}Al_{1\pm x}$ and $EuAu_{1\pm x}Al_{1\pm x}$ with higher gold content. The crystal chemical details are discussed for EuAuAl and LuAuAl.

Keywords: *A. Rare earth intermetallic; B. Crystal chemistry; C. Structural switch; D. Site occupancy; E. Valence electron concentration; F. X-ray diffraction*

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I. Introduction

The equiatomic ternary *RT*Al compounds (*R* = Sc, Y and rare earth elements, *T* = Cr, Fe, Ni, Cu, Ru Pd, Ag, Pt, Au) have been investigated in the last fifty years with respect to their structural chemistry and physical properties. Today more than 50 ternary *RT*Al compounds are known [1-15]. They crystallize with ordered superstructures of the aristotype AlB_2 [5]. Among the AlB_2 superstructures, the orthorhombic TiNiSi type [16] and hexagonal ZrNiAl type structures [17] are most frequently observed. In both the TiNiSi type and the ZrNiAl type structures, the *T* and *X* atoms built up an ordered three-dimensional [*TX*] polyanion in which the rare earth atoms fill cavities. Recently AAuAl (A = Ca, Sc, Ti) compounds were reported in different structure types: ortho-rhombic TiNiSi type CaAuAl; hexagonal Mg_2Ga type ScAuAl (a distorted superstructure of Fe_2P type); and hexagonal Ni_2In type TiAuAl [15]. Property investigations also have been carried out along with extensive structural works on these materials. EuAuAl exhibits antiferromagnetic ordering at T_N ~ 50 K [12]. ^{27}Al and ^{45}Sc magic angle spinning (MAS) and static NMR spectroscopic investigations have been carried out for Sc*T*Al, (*T* = Cr, Ru, Ag, Re, Pt, Au) [14].

In continuations of systematic studies of equiatomic *RET*Mg [19], *RET*Zn [20] and *RET*Cd [21] compounds we have now investigated the *RE*AuAl series in more detail. So far only powder X-ray diffraction data of *RE*AuAl [12] and crystal structure data of YbAuAl [13] have been published. Herein we focus on synthesis and crystal structural determination of *RE*AuAl (*RE* = Y, Eu, Lu) compounds. They were characterized by both powder and single crystal X-ray diffraction. YAuAl and EuAuAl phases crystallize with an orthorhombic TiNiSi type structure while LuAuAl with smaller size rare earth element adopts a hexagonal ZrNiAl type structure.

II. Experimental

2.1. Syntheses

Starting materials for the preparation of the *RE*AuAl (*RE* = Y, Eu, Lu) samples were the rare earth elements (Johnson Matthey or Kelpin), gold wire (Degussa-Hüls) and pieces of an aluminum rod (Koch chemicals), all with stated purities better than 99.9%. In the first step, pieces of the rare earth ingot were arc-melted [22] under argon (ca. 700 mbar) to small buttons. The argon was purified before with molecular sieves, silica gel and titanium sponge (900 K). The elements (1:1:1 atomic ratio) were then sealed in tantalum tubes under an argon pressure of 800 mbar. The tantalum tubes were placed in a water-cooled sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 2.5/300) [23]. The ampoules were rapidly heated to

1600 K and kept at the temperature for 5 min, followed by an annealing period of 4 hours at 1070 K. The temperature was controlled through a Sensor Therm Metis MS09 pyrometer with an accuracy of ±30 K. The samples were then quenched by switching off the power supply. Later the tantalum ampoules were sealed in a silica tube and annealed at 1070 K for two weeks. The silvery brittle samples could easily be separated from the tantalum tubes. No reaction with the container material was evident. The polycrystalline samples were stable in air over months. Single crystals exhibited metallic luster while ground powders were dark gray.

2.2. EDX analyses

The single crystals investigated on the diffractometer were studied by energy dispersive analyses of X-rays (EDX) using a Leica 420i scanning electron microscope with the rare earth trifluorides, Au and Al as standards. The crystals (mounted on quartz fibers) were first coated with a thin carbon film to ensure conductivity. The semi-quantitative analyses were in approximate agreement with the starting compositions. No impurity elements heavier than sodium (detection limit of the instrument) have been detected.

2.3. X-ray powder diffraction

The polycrystalline samples with the nominal compositions *RE*AuAl (*RE* = Y, Eu, Lu) were all characterized through Guinier powder patterns (Cu $K\alpha_1$ radiation, α-quartz: a = 491.30 and c = 540.46 pm as internal standard). The Guinier camera was equipped with an imaging plate technique (Fuji-film, BAS-READER 1800). The lattice parameters (Table 1) were obtained from least-squares refinements. The correct indexing was ensured through a comparison of the experimental patterns with calculated ones [24] using the atomic positions obtained from the structure refinements.

2.4. Single crystal X-ray data

Irregularly shaped single crystals were isolated from the crushed samples of YAuAl, EuAuAl and LuAuAl. They were glued to quartz fibers and investigated on a Buerger precession camera (white Mo radiation, Fuji-film imaging plate) in order to check their quality for intensity data collection. The data sets were collected at room temperature by use of two four-circle diffractometers (CAD4) with graphite monochromatized Mo$K\alpha$ (71.073 pm) or Ag$K\alpha$ (56.086 pm) radiation and scintillation counters with pulse height discrimination. Scans were taken in the ω/2θ mode. Empirical absorption corrections were applied on the basis of Ψ-scan data, accompanied by spherical absorption corrections. The crystallographic data of *RE*AuAl (*RE* = Y, Eu, Lu) are given in Tables 2 and 3.

III. Results and Discussion

3.1. Structure Refinements

The data sets of YAuAl and EuAuAl were compatible with the centrosymmetric space group *Pnma* in agreement with YbAuAl [13]. Analyses of the LuAuAl diffractometer data sets showed hexagonal lattices and no further systematic extinctions in agreement with the non-centrosymmetric space group space group $P\bar{6}2m$, since isotypism with ZrNiAl was already evident from the powder diffraction data [12]. The atomic parameters of YbAuAl [13] were taken as starting values for YAuAl and EuAuAl structural refinement. They were refined using SHELXL–97 (full-matrix least-squares on F^2) [25, 26] with anisotropic atomic displacement parameters for all atoms. These refinements showed significant residual electron densities. Since the *RE*AuMg series [27] revealed Au / Mg mixing for some compounds and all occupancy parameters for the present crystals were refined in a separate series of least-squares cycles. All rare earth sites proved to be fully occupied within two standard deviations. We observed Au / Al mixing with an excess of gold for YAuAl and EuAuAl compounds. These mixed occupancies were refined as a least-squares variable in the final cycles leading to the compositions listed in Tables 2 and 3. Hexagonal LuAuAl was refined with the setting of α-LuPdZn [28]. Refinement of the correct absolute structure for the LuAuAl was ensured through calculation of the Flack parameter [29, 30]. The final difference electron-density syntheses were flat. The results of the structure refinements for *RE*AuAl (*RE* = Y, Eu, Lu) are summarized in Tables 2 and 3.

3.2. Crystal Chemistry

The equiatomic ternary compounds *RE*AuAl (*RE* = Y, Eu, Lu) were synthesized from the elements and structurally characterized on the basis of powder and single crystal X-ray diffraction. So far from this series only powder X-ray diffraction data have been published for *RE*AuAl [12] and crystal structure data for YbAuAl [13]. Recently AAuAl (A = Ca, Sc, Ti) compounds were reported with consecutively increasing valence electron concentration (16−18 e^-/fu) and decreasing atomic radius crystallize in different structure types: orthorhombic TiNiSi type CaAuAl; hexagonal Mg_2Ga type ScAuAl (a distorted superstructure of Fe_2P type); and hexagonal Ni_2In type TiAuAl [15].

Among the *RE*AuAl (*RE* = Y, Eu, Lu) series we observe a switch in structure type as a consequence of the size of the rare earth element. All LnAuA1 members with the exception of LuAuA1 adopt the ordered TiNiSi structure, whereas LuAuA1 crystallizes in the ZrNiA1 structure [12, 13]. The metallic radius of Lu (R_{Lu} = 1.73 Å) is smaller than that of the other lanthanides (Ln = Y, Ce to Yb), which vary from 1.75−2.04 Å so that atomic size seems to play an important factor in the structural variation of LnAuAl. LuAuA1 crystallizes with the hexagonal ZrNiAl type structure [18], space group space group $P\bar{6}2m$, while yttrium and other larger rare earth elements, along with divalent europium and ytterbium (where the half-filled and filled *f* shells also lead to larger rare earth cations) adopt the orthorhombic TiNiSi type [13, 17], space group *Pnma*. This is different to the series *RE*AuMg [19] and *RE*AuCd [21], where only the divalent europium and ytterbium compounds crystallize with the TiNiSi type. In case of the series *RE*AuZn [20] the larger size lanthanides (Ln = La - Tb and Yb) crystallize with the TiNiSi type while smaller size lanthanides (Ln = Y, Dy-Tm and Lu) adopt hexagonal ZrNiAl type structure. In contrast, the trivalent stannides *RE*AuSn also show a switch in structure type with the large rare earth metals they crystallize with the NdPtSb type and those with the small rare earth elements adopt the cubic MgAgAs structure [31, 32].

The single crystal studies on YAuAl and EuAuAl showed deviations from the ideal composition *i.e.*, $YAu_{1.11}Al_{0.89}$ and $EuAu_{1.05}Al_{0.95}$ with higher gold content. LuAuAl exhibited no Al / Au mixing. The largest deviation was observed for $YAu_{1.11}Al_{0.89}$. In the *RE*AuMg series the homogeneity ranges are much smaller [19]. Seven representatives of the *RE*AuZn series showed deviations from the ideal composition [20]. Single crystal data of the *RE*AuCd compounds gave no hint for gold cadmium mixing [21].

The Al / Au mixing leads to small discrepancies between the lattice parameters refined from the Guinier powder data and those obtained on the diffractometers ((Table 1). The powder data reflect the bulk samples in which most domains are close to the ideal composition.

Since the crystal chemical details of TiNiSi and ZrNiAl type intermetallics has been repeatedly described [5, 33, and refs. therein], herein we only briefly discuss the structures of EuAuAl and LuAuAl. The interatomic distances (exemplarily for $EuAu_{1.05}Zn_{0.95}$ and LuAuAl) are listed in Table 4. The near-neighbor coordination of the respective rare earth sites are presented in Fig. 1 together with relevant interatomic distances. The shortest interatomic distances occur between Au and Al with the ranges 268–274 pm for EuAuAl and 266–275 pm for LuAuAl. These distances are in good agreement with Au‑Al distances in YbAuAl [13]. These shortest distances are consistent with the idea of a three-dimensional infinite $[AuAl]^{\delta-}$ polyanion. The europium atoms (CN=16) occupy the voids of Au / Al framework in TiNiSi type EuAuAl whereas lutetium atoms (CN=17) occupy the hexagonal voids of Au / Al framework in ZrNiAl type LuAuAl.

Valence electron concentrations (VECs), which are evaluated as the sum of the total number of valence ($s + p + d$) electrons per formula unit ($e-/fu$) are YAuAl (17$e-/fu$), EuAuAl (16$e-/fu$), LuAuAl (17$e-/fu$). Despite different values of VECs, YAuAl and EuAuAl adopt TiNiSi type structure while LuAuAl (VECs = 17$e-/fu$) favors ZrNiA1 type structure.

The cell volume (V) for $YAu_{1.11}Al_{0.89}$ and $EuAu_{1.05}Al_{0.95}$ are 0.2464 nm^3 and 0.2714 nm^3 respectively while for LuAuAl (V) = 0.1776 nm^3. This structural variation from TiNiSi type structure (EuAuAl) to ZrNiA1 type (LuAuAl) is related to the chemical pressure effects, indicating larger unit cells favoring the orthorhombic TiNiSi-type structure whereas smaller unit cells favoring the hexagonal ZrNiA1 type structure. Therefore, size is playing an important role in this structural variation.

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Table 1 Lattice parameters of *RE*AuAl (*RE* = Y, Eu, Lu).

Compound	*a* (pm)	*b* (pm)	*c* (pm)	*V* (nm^3)	Ref.
YAuAl	715.58(6)	444.38(4)	774.07(5)	0.2462	[12]
YAuAl	713.03(10)	445.61(8)	774.89(13)	0.2462	This work
$YAu_{1.107(3)}Al_{0.893(3)}$*	712.88(10)	445.80(10)	775.32(10)	0.2464	This work
EuAuAl	754.29(8)	464.59(4)	773.45(7)	0.2710	[12]
EuAuAl	752.64(12)	464.38(9)	776.25(12)	0.2713	This work
$EuAu_{1.045(3)}Al_{0.955(3)}$*	752.29(10)	464.43(10)	776.69(10)	0.2714	This work
LuAuAl	710.33(4)	= *a*	405.88(4)	0.1774	[12]
LuAuAl	709.71(11)	= *a*	407.06(5)	0.1776	This work
LuAuAl*	709.62(10)	= *a*	407.27(8)	0.1776	This work

(* single crystal data)

Table 2 Crystallographic data and structure refinements of *RE*AuAl (*RE* = Y, Eu, Lu).

Refined composition	$YAu_{1.107(3)}Al_{0.892(3)}$	$EuAu_{1.045(3)}Al_{0.955(3)}$	LuAuAl
Space group	*Pnma*	*Pnma*	$P\bar{6}2m$
Z	4	4	3
Lattice parameters	Table 1	Table 1	Table 1
Molar mass, g/mol	331.13	383.56	398.92
Crystal size, μm^3	20 × 30 × 40	25 × 35 × 50	20 × 35 × 45
Calculated density, g cm^{-3}	8.93	9.39	11.19
Transm. ratio, max / min	0.1286 / 0.0001	0.9306 / 0.1241	0.5902 / 0.2526
Radiation	Mo K_α	Mo K_α	Mo K_α
[λ, pm]	71.073	71.073	71.073
Absorption coeff., mm^{-1}	89.24	79.26	103.28
F(000), e	552	632	489
θ-range, deg.	4 – 27	4 – 30	3 – 35
Range in *hkl*	±8, ±5, ±9	±10, ±6, ±10	-11/+9, ±11, ±6
Total no. reflections	1884	2967	2731
Independent reflections / R_{int}	290 / 0.1259	445 / 0.0638	323 / 0.1379
Reflections with $I \geq 2\sigma(I)$ / R_σ	262 / 0.0603	406 / 0.0306	320 / 0.0559
Data / parameters	290 / 21	445 / 21	323 / 14
Goodness-of-fit on F^2	1.089	1.117	1.159
$R1$, $wR2$ for $I \geq 2\sigma(I)$	0.0316, 0.0773	0.0325, 0.0792	0.0277, 0.0722
$R1$, $wR2$ for all data	0.0364, 0.0807	0.0374, 0.0813	0.0282, 0.0724
Extinction coefficient	0.0039(10)	0.0033(5)	0.0140(11)
Largest diff. peak / hole, e$Å^{-3}$	4.48 / –3.44	4.07 / –2.64	4.72 / –3.64

Table 3 Atomic coordinates and anisotropic displacement parameters (pm^2) for *RE*AuAl (*RE* = Y, Eu, Lu). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$; $U_{23} = 0$; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{13}/U_{12}	U_{eq}
$YAu_{1.107(3)}Al_{0.892(3)}$								
Y	0.5065(2)	1/4	0.2974(2)	74(8)	78(9)	60(8)	12(5)	71(5)
Au	0.7880(1)	1/4	0.5915(1)	110(5)	69(5)	73(4)	-9(2)	84(4)
0.892(3) Al + 0.108(3) Au	0.1918(5)	1/4	0.5804(4)	255(26)	94(22)	79(19)	13(11)	143(15)
$EuAu_{1.045(3)}Al_{0.955(3)}$								
Eu	0.5152(1)	1/4	0.3199(1)	79(4)	121(4)	79(4)	14(2)	93(2)
Au	0.7986(1)	1/4	0.6108(1)	81(3)	118(3)	114(3)	-22(2)	104(2)
0.958(3) Al + 0.042(3) Au	0.1607(6)	1/4	0.5715(5)	230(27)	140(20)	23(21)	28(14)	131(16)
LuAuAl								
Lu	0.5843(1)	0	0	46(3)	31(4)	77(3)	16(2)	53(2)
Au1	0	0	0	50(3)	50(3)	45(4)	25(2)	49(2)
Au2	1/3	2/3	1/2	66(3)	66(3)	87(3)	33(1)	73(2)
Al	0.2420(10)	2/3	1/2	20(19)	23(26)	55(20)	11(13)	33(10)

Table 4 Interatomic distances (pm) in the structures of *RE*AuAl (*RE* = Y, Eu, Lu). All distances within the first coordination shells are listed. Standard deviations are all equal or smaller than 1.2 pm.

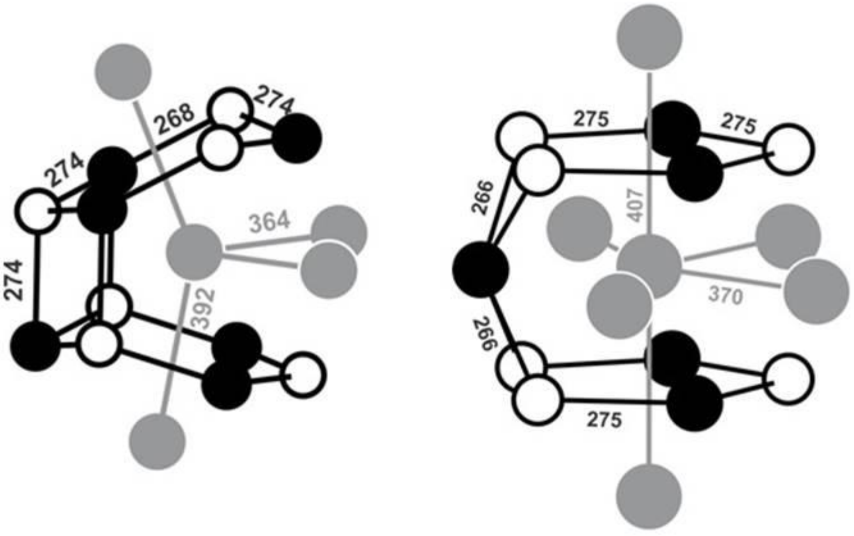
$EuAu_{1.045(3)}Al_{0.955(3)}$

Eu:	1	Au	310.6
	2	Au	316.1
	1	Al	323.0
	2	Al	329.6
	1	Al	330.7
	2	Au	335.5
	2	Al	347.1
	2	Eu	364.1
	1	Au	372.0
	2	Eu	391.7
Au:	1	Al	267.5
	2	Al	273.7
	1	Al	274.2
	1	Eu	310.6
	2	Eu	316.1
	1	Eu	335.5
Al:	1	Au	267.5
	2	Au	273.7
	1	Au	274.2
	1	Eu	323.0
	2	Eu	329.6
	1	Eu	330.7
	2	Eu	347.1

LuAuAl

Lu:	4	Au2	294.9
	1	Au1	295.0
	2	Al	316.9
	4	Al	327.5
	4	Lu	369.7
	2	Lu	407.1
Au1:	6	Al	266.3
	3	Lu	295.0
Au2:	3	Al	274.8
	6	Lu	294.9
Al:	2	Au1	266.3
	2	Au2	274.8
	2	Al	297.5
	2	Lu	316.9
	4	Lu	327.5
	2	Al	407.1

FIGURE CAPTIONS



EuAuAl **LuAuAl**

Figure 1 Coordination of the Rare earth atoms in EuAuAl and LuAuAl.