

Sr₂Au₆Al₃ and Eu₂Au₆Al₃ – First Representatives of the Sr₂Au₆Zn₃ Type with Aluminum Triangles

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The aluminides Sr₂Au₆Al₃ and Eu₂Au₆Al₃ were synthesized by melting the elements in sealed tantalum tubes in a muffle or induction furnace. The samples were characterized by powder and single-crystal X-ray diffraction: Sr₂Au₆Zn₃ type, $R\bar{3}c$, $a = 845.1(1)$, $c = 2177.2(3)$ pm, $wR2 = 0.0263$, 520 F^2 values, 20 variables for Sr₂Au_{6.18(1)}Al_{2.82(1)}, and $a = 838.0(1)$, $c = 2177.1(7)$ pm, $wR2 = 0.0276$, 510 F^2 values, 19 variables for Eu₂Au₆Al₃. The gold atoms build up diamond-related networks of slightly distorted tetrahedra in the stacking sequence of the 6R polytype (289–296 pm Au–Au in Eu₂Au₆Al₃). The voids left by this network are filled in an ordered manner by strontium (europium) atoms and the rare motif of Al₃ triangles (286 pm Al–Al in Eu₂Au₆Al₃). The Al₃ triangles in Sr₂Au_{6.18(1)}Al_{2.82(1)} show a small degree of Al/Au mixing.

Key words: Aluminum, Crystal Structure, Stuffed Diamond Network, Gold, Europium, Strontium

Introduction

Intermetallic aluminum compounds have intensively been studied in the last decades during fundamental and applied research in the field of modern light weight alloys. Especially the binary T -Al as well as the ternary RE - T -Al systems (T = transition metal; RE = rare earth element) have thoroughly been investigated, and the many crystallographic data are compiled in the Pearson data base [1]. Since aluminum has a comparatively high liquidus range (melting point 933 K, boiling point 2740 K [2]), many of such aluminides are accessible *via* arc-melting. The aluminum-rich phases can be prepared in single-crystalline form through the self-flux technique [3]. Most of the binary and ternary aluminides have higher corrosion stability

than aluminum itself, and the remaining flux can be dissolved in diluted hydrochloric acid.

Aluminides exhibit a versatile crystal chemistry. The aluminum-rich phases show three-dimensional networks formed by the aluminum atoms with ranges of Al–Al distances that resemble *fcc* Al (12×286 pm [4]). The other metal atoms are located in voids of different size within the complex aluminum substructure. A rare example of a two-dimensional aluminum substructure is AlB₂-type ThAl₂ [5] with honey-comb networks (253 pm Al–Al). Further *dilution* of the aluminum substructure by other metals leads to isolated aluminum atoms, *i. e.* no Al–Al bonding.

In between the extreme bonding situations, *i. e.* extended networks *vs.* isolated aluminum atoms, one observes the rare motif of Al₄ tetrahedra which occurs in the rare earth-rich phases RE_4TAl (T = Ru, Rh, Ir) [6] with cubic Gd₄RhIn-type structure [7]. These Al₄ tetrahedra are surrounded exclusively by rare earth atoms. The Al–Al distances are 300 pm in Gd₄RhAl. During our recent phase analytical investigations of AE - T - X (AE = Ca, Sr, Ba; T = electron-rich transition metal; X = Al, Ga, In, Mg, Cd, Zn) systems [8–11] we observed another aluminum species. The new aluminides Sr₂Au₆Al₃ and Eu₂Au₆Al₃ crystallize with the rhombohedral Sr₂Au₆Zn₃-type structure with Al₃ triangles. The synthesis and structure of these phases are reported herein.

Experimental

Synthesis

Starting materials for the synthesis of the Sr₂Au₆Al₃ and Eu₂Au₆Al₃ samples were sublimed ingots of strontium (Aldrich, > 99%) and europium (Johnson Matthey, > 99.9%), pieces of a gold bar (Heraeus, > 99.9%) and aluminum chips (Koch Chemicals, > 99.99%). The strontium granules were cut into smaller pieces under dry paraffin oil and subsequently washed with *n*-hexane. These pieces as well as the europium ingots were kept in Schlenk tubes under argon prior to the reaction. The elements were weighed in the ratio 3 : 7.2 : 3 in order to prevent formation of the phase SrAu_{4+x}Al_{3-x} and then arc-welded [12] in tantalum tubes under an argon pressure of *ca.* 800 mbar. Argon was purified with titanium sponge (900 K), silica gel, and molecular sieves. The strontium-containing tantalum ampoule was

	Sr ₂ Au _{6.18} (1)Al _{2.82} (1)	Eu ₂ Au ₆ Al ₃	Table 1. Crystal data and structure refinement for Sr ₂ Au _{6.18} Al _{2.82} and Eu ₂ Au ₆ Al ₃ , space group $R\bar{3}c$, $Z = 6$.
Empirical formula	Sr ₂ Au _{6.18} (1)Al _{2.82} (1)	Eu ₂ Au ₆ Al ₃	
Formula weight, g mol ⁻¹	1469.25	1566.66	
Unit cell dimensions (single-crystal data)			
<i>a</i> , pm	844.43(4)	837.73(3)	
<i>c</i> , pm	2168.9(1)	2177.80(9)	
<i>V</i> , nm ³	1.3394	1.3236	
Unit cell dimensions (Guinier powder data)			
<i>a</i> , pm	845.1(2)	838.0(1)	
<i>c</i> , pm	2177.2(3)	2177.1(7)	
<i>V</i> , nm ³	1.3466	1.3240	
Calculated density, g cm ⁻³	10.93	11.79	
Crystal size, μm ³	20 × 30 × 45	20 × 50 × 60	
Transm. ratio (max/min)	0.177/0.084	–	
Absorption coefficient, mm ⁻¹	113.2	113.5	
<i>F</i> (000), e	3607	3834	
θ range, deg	3° to 32°	3° to 32°	
Range in <i>hkl</i>	±12, ±12, ±32	±12, ±12, ±31	
Total no. reflections	4383	10279	
Independent reflections/ <i>R</i> _{int}	520/0.0479	510/0.0628	
Reflections with <i>I</i> > 2 σ (<i>I</i>)/ <i>R</i> _{σ}	430/0.0284	487/0.0165	
Data/parameters	520/20	510/19	
Goodness-of-fit on <i>F</i> ²	0.964	1.286	
<i>R</i> 1/ <i>wR</i> 2 for <i>I</i> > 2 σ (<i>I</i>)	0.0188/0.0255	0.0146/0.0274	
<i>R</i> 1/ <i>wR</i> 2 for all data	0.0280/0.0263	0.0160/0.0276	
Extinction coefficient	0.00013(1)	0.0002(1)	
Largest diff. peak/hole, e Å ⁻³	1.44/–1.76	1.91/–1.25	

sealed in a silica tube under vacuum. The reaction was carried out in a resistance furnace by heating to 1300 K, keeping at that temperature for 10 min and finally for 8 h at 800 K. Subsequently the sample was cooled to room temperature. The tantalum ampoule with europium, gold and aluminum was placed in the water-cooled sample chamber of an induction furnace [13] (Kontron Roto-Melt). The tube was heated to ca. 1300 K, kept at that temperature for 5 min and cooled down to room temperature at a rate of 35 K min⁻¹. The temperature was controlled by a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. Afterwards the sample was annealed for 4 d at 670 K. The obtained polycrystalline samples showed metallic luster and were stable in air over weeks.

X-Ray diffraction

The two polycrystalline samples were characterized by Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) using CuK _{α 1} radiation and α -quartz (*a* = 491.30, *c* = 540.46 pm) as an internal standard. Least-squares refinements led to the rhombohedral lattice parameters listed in Table 1. Comparison of the experimental patterns with calculated [14] ones assured correct indexing.

Irregularly shaped single crystals of Sr₂Au₆Al₃ and Eu₂Au₆Al₃ were selected from the crushed annealed samples and glued to quartz fibers using bees wax. They were investigated by Laue photographs on a Buerger camera

(white molybdenum radiation, imaging plate technique, Fujifilm, BAS-1800) in order to check the crystal quality. Intensity data were collected at room temperature by use of a Stoe IPDS-II imaging plate diffractometer (graphite-monochromatized MoK _{α} radiation) in oscillation mode. A numerical absorption correction was applied to the Sr₂Au₆Al₃ data set. Crystallographic details are listed in Table 1.

EDX analyses

The single crystals investigated on the diffractometers were studied by EDX using a Zeiss EVO MA10 scanning electron microscope with SrF₂, EuF₃, Au, and Al₂O₃ as standards for the semi-quantitative measurements. No impurity elements heavier than sodium (detection limit of the instrument) were observed. Due to the irregular surface of the crystals (conchoidal fracture) a reliable determination of absolute compositions was not possible.

Structure refinements

Isotopy of the aluminides Sr₂Au₆Al₃ and Eu₂Au₆Al₃ with the recently discovered rhombohedral structure type Sr₂Au₆Zn₃ [10] was already evident from the Guinier powder data. Both diffractometer data sets showed rhombohedral lattices, and the systematic extinctions were compatible with space group $R\bar{3}c$. The atomic parameters of the zinc compound were taken as starting values, and the struc-

tures were refined with anisotropic displacement parameters for all atoms with SHELXL-97 (full-matrix least-squares on F_o^2) [15, 16]. To check for deviations from the ideal composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites of the $\text{Eu}_2\text{Au}_6\text{Al}_3$ crystal were fully occupied within two standard deviations. The aluminum site of the strontium crystal showed slightly enhanced scattering power. In the final cycles this site was refined with Al/Au mixing and has led to the composition $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ for the investigated crystal. The final difference Fourier synthesis revealed no residual peaks. The refined atomic positions, displacement parameters, and interatomic distances are given in Tables 2–4.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-427020 ($\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$) and CSD-427021 ($\text{Eu}_2\text{Au}_6\text{Al}_3$).

Table 2. Atomic positions of $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ and $\text{Eu}_2\text{Au}_6\text{Al}_3$, space group $R\bar{3}c$, $Z = 6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The Al position in $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ shows a mixed occupancy of 93.9(3) % Al + 6.1(3) % Au.

Atom	Wyckoff site	x	y	z	U_{eq}
$\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$					
Sr	12c	0	0	0.08977(4)	116(2)
Au	36f	0.37291(3)	0.35482(3)	0.15150(1)	122(1)
Al/Au	18e	0.1846(3)	x	1/4	152(7)
$\text{Eu}_2\text{Au}_6\text{Al}_3$					
Eu	12c	0	0	0.08891(2)	90(1)
Au	36f	0.37321(2)	0.35388(2)	0.15093(1)	93(1)
Al	18e	0.1967(2)	x	1/4	79(3)

Table 3. Anisotropic displacement parameters (pm^2) of $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ and $\text{Eu}_2\text{Au}_6\text{Al}_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$; $U_{13} = U_{23} = 0$. Note that the aluminum position in $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ shows a mixed occupancy of 93.9(3) % Al + 6.1(3) % Au.

Atom	Wyckoff site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$							
Sr	12c	113(3)	U_{11}	123(4)	$1/2U_{11}$	0	0
Au	36f	110(1)	128(1)	113(1)	49(1)	10(1)	20(1)
Al/Au	18e	233(10)	U_{11}	83(8)	189(9)	$-U_{23}$	8(3)
$\text{Eu}_2\text{Au}_6\text{Al}_3$							
Eu	12c	79(1)	U_{11}	110(2)	$1/2U_{11}$	0	0
Au	36f	81(1)	94(1)	93(1)	36(1)	15(1)	20(1)
Al	18e	87(6)	U_{11}	71(9)	49(7)	$-U_{23}$	4(4)

Discussion

The aluminides $\text{Sr}_2\text{Au}_6\text{Al}_3$ and $\text{Eu}_2\text{Au}_6\text{Al}_3$ crystallize with the $\text{Sr}_2\text{Au}_6\text{Zn}_3$ -type structure [10]. When we

Table 4. Interatomic distances (pm) in the structures of $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ and $\text{Eu}_2\text{Au}_6\text{Al}_3$. Standard deviations are given in parentheses. All distances within the first coordination spheres are listed. Note that the aluminum position in $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ shows a mixed occupancy of 93.9(3) % Al + 6.1(3) % Au.

		$\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$	$\text{Eu}_2\text{Au}_6\text{Al}_3$	
Sr/Eu:	3 Au	324.7(1)	322.4(1)	
	3 Au	325.9(1)	326.3(1)	
	3 Au	335.4(1)	333.5(1)	
	3 Al	361.3(2)	351.1(1)	
	3 Au	361.3(1)	361.2(1)	
	Au:	1 Al	261.1(1)	257.4(1)
1 Al		262.2(1)	260.0(1)	
1 Al		276.9(1)	275.9(2)	
2 Au		289.1(1)	288.6(1)	
1 Au		297.4(1)	294.4(1)	
1 Au		297.5(1)	295.8(1)	
Al:		2 Au	261.1(1)	257.4(1)
		2 Au	262.2(1)	260.0(2)
	2 Al	270.0(4)	285.5(4)	
	2 Au	276.9(1)	275.9(1)	

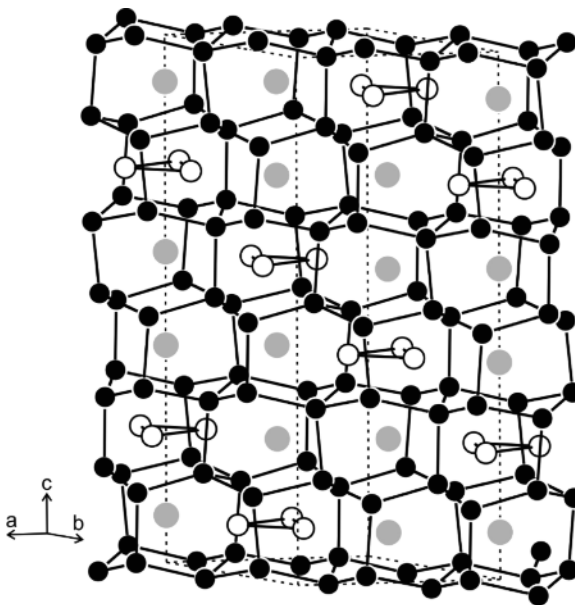


Fig. 1. View of the $\text{Eu}_2\text{Au}_6\text{Al}_3$ structure approximately along the $[120]$ direction. Europium, gold and aluminum atoms are drawn as medium gray, black and open circles, respectively. The diamond-related gold substructure and the Al_3 triangles are emphasized.

quote interatomic distances in the following discussion we only refer to the europium compound. The gold atoms build up diamond-related tetrahedral substructures which resemble the 6R polytype of diamond [17]. The Au–Au distances within the gold substructure of $\text{Eu}_2\text{Au}_6\text{Al}_3$ range from 289 to 296 pm, slightly longer than in the orthorhombically distorted tetrahedral gold substructure of EuAu_2 (273–280 pm) [18]. All of these gold substructures derive from the aristotype AlB_2 by group-subgroup relations [10, 19].

The large cavities left by the tetrahedral gold substructure are filled in an ordered manner by the strontium (europium) atoms and Al_3 triangles, a rare structural motif (Fig. 1). The europium atoms are directly bonded to the gold atoms with Eu–Au distances ranging from 322–334 pm, similar to EuAuGe (314–335 pm) [20] and EuAuSn (322–352 pm) [21]. The Al–Al distance within the Al_3 triangles of 286 pm is similar to that in *fcc* Al (12×286 pm) [4]. The molecular counterpart to this intermetallic compound is the radical $(t\text{Bu}_3\text{Si})_4\text{Al}_3^\bullet$ [22] with a slightly dis-

torted triangle and Al–Al distances of 270, 274 and 278 pm.

While the triangles are fully ordered in the europium compound, we find a small degree of Al/Au mixing for $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$. Similar mixing has also been observed for $\text{Ba}_3\text{Ag}_{14.6}\text{Al}_{6.4}$ [23] which crystallizes with its own hexagonal structure type, as well as for solid solutions $\text{Ba}_2\text{Au}_6(\text{Au},T)_3$ ($T = \text{Zn}, \text{Cd}, \text{Ga}, \text{In}, \text{Sn}$) [24] and $\text{Sr}_2\text{Au}_6(\text{Au},T)_3$ ($T = \text{Zn}, \text{Ga}$) [10, 25]. The Al/Au mixing in $\text{Sr}_2\text{Au}_{6.18}\text{Al}_{2.82}$ is also expressed by the smaller lattice parameters of the single crystal and the shorter Al/Au–Al/Au distance of 270 pm in the triangle, a consequence of strong Al–Au bonding.

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