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Different stacking of the gold and silicon atoms in the phases RAuSi (R≡Sc, Y, Lu)

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Abstract

The structures of ScAuSi, YAuSi and LuAuSi were determined by single-crystal diffractometry. ScAuSi, hP6, hexagonal $P\bar{6}m2$ (no. 187), $a=4.212(1)$ Å, $c=6.803(2)$ Å, $Z=2$, $R=0.030$ using 85 reflections, represents a new ternary ordered type. YAuSi, hP6, hexagonal $P6_3mc$ (no. 186), $a=4.288(2)$ Å, $c=7.546(3)$ Å, $Z=2$, $R=0.039$ using 66 reflections, is isotypic with LiGaGe (ternary ordered derivative of the $CaIn_2$ structure). LuAuSi, isotypic with ScAuSi, $a=4.267(2)$ Å, $c=7.151(3)$ Å, was refined to $R=0.052$ using 90 reflections. In both ScAuSi and YAuSi structures trigonal prisms of scandium or yttrium sharing their lateral faces are stacked along the c axis. The gold and silicon atoms forming rumpled layers centre the prisms in an ordered way. The difference between the two structures consists in the different stacking of these layers along the c axis. In YAuSi atoms of gold in a layer alternate with atoms of silicon in the subsequent layer, and vice versa; in ScAuSi the layers become equally oriented so that Au–Au and Si–Si pairs are formed.

1. Introduction

Many intermetallic ternary compounds of the rare earths (R) exist with equiatomic composition 1:1:1 [1]. Several of them have crystal structures derived from the binary AlB_2 type by replacing the B atoms with two atomic partners of the rare earth metal. However, as they were mostly investigated by X-ray powder methods, the accurate atomic coordinates and especially the ordered or disordered occupation of the sites often remain undetermined.

Concerning ternary silicides with the group 11 elements, the RCuSi phases were studied by both X-ray [2] and neutron [3] diffraction methods and a low temperature ordered modification with Ni_2In derivative structure was found for all rare earths and yttrium, excluding europium. The RAgSi phases with R≡Sm, Gd, Dy, Er, Tm, Yb, Lu, Y [4] exhibit an ordered arrangement of the silver and silicon sites according to the ZrNiAl type. The same ZrNiAl structure is adopted also by ScCuSi [5] in the stoichiometric 1:1:1 composition.

As no data are present in the literature for the corresponding equiatomic phases with gold, in this work we examined three representatives of the RAuSi family and determined their crystal structures by single-crystal X-ray methods.

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2. Experimental details

The compounds were prepared using scandium (99.99%), yttrium (99.9%), lutetium (99.8%), gold and silicon (99.999%). Stoichiometric amounts of the components were arc melted under an argon atmosphere in the case of ScAuSi and LuAuSi samples, while YAuSi was melted in a semilevitation furnace. The ScAuSi and YAuSi samples were then annealed in quartz tubes under vacuum for a week at 1013 K and 973 K respectively.

Single crystals of ScAuSi (needle, 0.03 mm × 0.03 mm × 0.07 mm), YAuSi (platelet, 0.03 mm × 0.08 mm × 0.08 mm) and LuAuSi (trigonal pyramid, 0.07 mm × 0.10 mm × 0.14 mm) were X-ray examined by means of an Enraf–Nonius CAD-4 automatic diffractometer, using graphite-monochromated Mo Kα radiation. Lattice parameters were obtained from 25 diffractometer-measured reflections. Details of the data collections are as follows: ScAuSi, ω–2θ scan mode up to $\sin\theta/\lambda = 0.7$ Å^{-1}, $-5 \leqslant h, k \leqslant 5$, $0 \leqslant l \leqslant 9$, 645 measured reflections, 89 independent reflections ($R_{\text{int}} = 0.080$); YAuSi, ω–θ scan mode up to $\sin\theta/\lambda = 0.65$ Å^{-1}, $-5 \leqslant h$, $k \leqslant 5$, $0 \leqslant l \leqslant 9$, 556 measured reflections, 71 independent reflections ($R_{\text{int}} = 0.118$); LuAuSi, ω–2θ scan mode up to $\sin\theta/\lambda = 0.7$ Å^{-1}, $-6 \leqslant h \leqslant 6$, $0 \leqslant k \leqslant 6$, $-10 \leqslant l \leqslant 10$, 726 measured reflections, 95 independent reflections ($R_{\text{int}} = 0.157$). No decay of the crystals was observed during the data collections. Both spherical and semiempirical absorption corrections based on the azimuthal scan data of top reflections were applied. The linear absorption coefficient and ratio between maximum and minimum transmission factors were 75.7 mm^{-1} and 1.8 for ScAuSi, 87.9 mm^{-1} and 7.2 for YAuSi, and 112.8 mm^{-1} and 2.6 for LuAuSi.

3. Crystal structure determinations

The three crystals were found to be hexagonal with $6/mmm$ Laue symmetry, very similar lattice constants and the same content of the unit cell ($Z = 2$). For ScAuSi, as no systematic absences were observed, a possible model was proposed in the space group $P\bar{6}m2$ (no. 187) and confirmed by refinement. Refinement of eight parameters including anisotropic thermal factors of the gold atom with weights $w = 1/\sigma^2\ (F_0)$ gave $R = 0.030$ for 85 reflections with $F_0 > 2\sigma(F_0)$. The maximum and minimum electron density in the final difference Fourier synthesis was 3.2 e$^-$ Å^{-3} and -4.6 e$^-$ Å^{-3} respectively. This structure is of a new type.

The YAuSi crystal exhibited systematic extinctions of hhl reflections with $l = 2n + 1$ consistent with the space groups $P6_3mc$ and $P6_3/mmc$. A model of the structure in the space group $P6_3mc$ (no. 186) taken from the LiGaGe type (ternary ordered derivative of the $CaIn_2$ structure) [1] was assumed. Refinement of eight parameters including anisotropic thermal factors of the yttrium and gold atoms using 66 reflections with $F_0 > 3\sigma(F_0)$ and weights $w = 1/[\sigma^2(F_0) + 0.0002F_0^2]$ gave $R = 0.039$. The maximum and minimum electron density in the final difference Fourier synthesis was 2.1 $e^- Å^{-3}$ and -1.9 $e^- Å^{-3}$ respectively.

The LuAuSi crystal had the same structure as ScAuSi. Refinement of nine parameters including anisotropic thermal factors of the lutetium and gold atoms with weights $w = 1/[\sigma^2(F_0) + 0.01F_0^2]$ gave $R = 0.052$ for 90 reflections with $F_0 > 3\sigma(F_0)$. The U_{11} factor of the gold atom exhibited a tendency to become slightly negative and was then fixed to 0. The poor quality of the crystal found after many trials from a poorly crystallized matrix could be responsible for both this anomaly and the relative high values of the maximum and minimum electron density in the final difference Fourier synthesis, 6.6 $e^- Å^{-3}$ and -8.2 $e^- Å^{-3}$ respectively. It has to be noted that the as-cast alloy of LuAuSi, from which the crystal was selected, and the same alloy after annealing at 1013 K for a week, exhibit different powder patterns, although some resemblance is still recognizable. So, the LuAuSi phase with ScAuSi structure can be considered as a high temperature phase.

The program used for the structure refinements was SHELX-76 [6] with atomic scattering factors and anomalous dispersion corrections taken from the *International Tables for X-ray Crystallography* [7].

Table 1 reports atomic coordinates and thermal parameters for ScAuSi, LuAuSi and YAuSi. In Table 2 are listed interatomic distances up to $d/\Sigma r = 1.11$, where d is the distance and Σr the sum of the corresponding metallic radii for coordination number 12.

Lists of structure factors can be obtained from the authors on request.

TABLE 1

Atomic coordinates and thermal parameters for ScAuSi, LuAuSi and YAuSi

		x	y	z	U_{11} ($Å^2$)	U_{33} ($Å^2$)
ScAuSi ($P\bar{6}m2$), $a = 4.212(1)$ Å, $c = 6.803(2)$ Å						
Sc1	1(b)	0	0	1/2	0.007(2)	
Sc2	1(a)	0	0	0	0.007(2)	
Au	2(i)	2/3	1/3	0.2158(2)	0.0042(4)	0.0090(6)
Si	2(h)	1/3	2/3	0.297(2)	0.007(2)	
LuAuSi ($P\bar{6}m2$), $a = 4.267(2)$ Å, $c = 7.151(3)$ Å						
Lu1	1(b)	0	0	1/2	0.007(2)	0.005(2)
Lu2	1(a)	0	0	0	0.004(1)	0.005(2)
Au	2(i)	2/3	1/3	0.2220(5)	0[a]	0.010(1)
Si	2(h)	1/3	2/3	0.295(4)	0.004(4)	
YAuSi ($P6_3mc$), $a = 4.288(2)$ Å, $c = 7.546(3)$ Å						
Y	2(a)	0	0	0[b]	0.017(1)	0.004(3)
Au	2(b)	1/3	2/3	0.234(1)	0.0128(7)	0.018(1)
Si	2(b)	1/3	2/3	0.775(2)	0.005(3)	

Estimated standard deviations are in parentheses. For the atoms anisotropically refined $U_{11} = U_{22} = 2U_{12}$ and $U_{13} = U_{23} = 0$.

[a] See text.

[b] Arbitrarily fixed.

TABLE 2

Interatomic distances (ångströms) in ScAuSi, LuAuSi and YAuSi up to $d/\Sigma r = 1.11$

ScAuSi			
Sc1–6Si	2.80(1)	Sc2–6Au	2.84(1)
–6Au	3.11(1)	–6Si	3.16(1)
–2Sc2	3.40(1)	–2Sc1	3.40(1)
Au–3Si	2.49(1)	Si–3Au	2.49(1)
–3Sc2	2.84(1)	–Si	2.76(3)
–Au	2.94(1)	–3Sc1	2.80(1)
–3Sc1	3.11(1)	–3Sc2	3.16(1)
LuAuSi			
Lu1–6Si	2.87(1)	Lu2–6Au	2.93(1)
–6Au	3.17(1)	–6Si	3.24(2)
–2Lu2	3.57(1)	–2Lu1	3.57(1)
Au–3Si	2.52(1)	Si–3Au	2.52(1)
–3Lu2	2.93(1)	–3Lu1	2.87(1)
–3Lu1	3.17(1)	–Si	2.93(5)
–Au	3.18(1)	–3Lu2	3.24(2)
YAuSi			
Y–3Si	3.00(1)	Au–3Si	2.49(1)
–3Au	3.04(1)	–3Y	3.04(1)
–3Au	3.19(1)	–3Y	3.19(1)
–3Si	3.23(1)		
–2Y	3.77(1)	Si–3Au	2.49(1)
		–3Y	3.00(1)
		–3Y	3.23(1)

Estimated standard deviations are in parentheses.

4. Discussion

The three examined phases exhibit a complete ordering of the three types of atoms on the different crystallographic sites. The structures of ScAuSi and YAuSi (LiGaGe type) are compared in Fig. 1. In both structures layers of rumpled hexagons of gold and silicon atoms are inserted between triangular nets of yttrium or scandium atoms. In YAuSi the hexagons are stacked along the *c* axis in such a way that a gold atom always alternates with a silicon atom in the subsequent rumpled layer at a distance much greater than the sum of their metallic radii. In ScAuSi the layers are equally oriented allowing Au–Au and Si–Si pairs to form at distances slightly greater than their metallic diameters. This particular feature modifies the coordinations of the atoms, which are, however, very similar in the two structures.

The gold (or silicon) atom is surrounded by a trigonal prism formed by the more electropositive atoms yttrium or scandium, with the lateral faces capped by three silicon (or gold) atoms. In the case of ScAuSi the presence of Au–Au and Si–Si pairs allows another gold (or silicon) atom emerging from a triangular face of the prism to be coordinated. It is clear that the

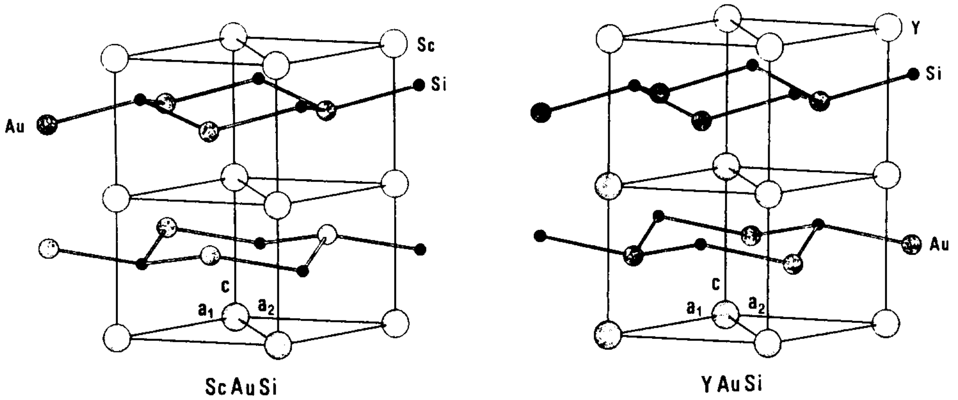

Fig. 1. Rumpled layers formed by hexagons of alternating gold and silicon atoms, which are differently stacked in the two structures of ScAuSi and YAuSi. Scandium or yttrium trigonal prisms surrounding the gold and silicon atoms are outlined.

ScAuSi structure can be realized only when the atoms forming the trigonal prism are small enough to allow the pair contacts through a triangular face. The scandium and lutetium atoms satisfy this requirement, while yttrium with a greater size adopts the LiGaGe structure.

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