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Crystal structures of the ternary cerium rhodium silicides $Ce_2Rh_{12}Si_7$ and $Ce_6Rh_{30}Si_{19}$

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Abstract

The crystal structures of the new compounds $Ce_2Rh_{12}Si_7$ and $Ce_6Rh_{30}Si_{19}$, extracted from an ingot of composition $Ce_{9.5}Rh_{56.9}Si_{33.6}$, were investigated by X-ray single crystal diffraction methods. The title compounds crystallize in the hexagonal space group $P6_3/m$ with unit cell parameters $a = 9.706(1)$ Å, $c = 3.8394(3)$ Å and $a = 15.698(2)$ Å, $c = 3.8571(4)$ Å, respectively. $Ce_2Rh_{12}Si_7$ and $Ce_6Rh_{30}Si_{19}$ represent members of a family of hexagonal structures with a short unit cell parameter $c \approx 3.7$ Å and with general formula $R_{n(n+1)}T_{6(n^2+1)}M_{4n^2+3}$, where R is the rare earth, T the transition metal, and M the element of the IV or V main group. $Ce_2Rh_{12}Si_7$ crystallizes with the $Ho_2Rh_{12}As_7$ type, ignoring the disordered arrangement of non-metal atoms on the c-axis. The structure of $Ce_6Rh_{30}Si_{19}$ is closely related to that of $Sc_6Co_{30}Si_{19}$.

Keywords: Cerium rhodium silicide; Crystal structure; $Ce_2Rh_{12}Si_7$; $Ce_6Rh_{30}Si_{19}$

1. Introduction

The ternary system Ce–Rh–Si has not yet been studied over the whole concentration range. Our investigation of the Ce–Rh–Si ternary system [1] led to the establishment of the new ternary intermetallic compounds $Ce_2Rh_{12}Si_7$ (I) and $Ce_6Rh_{30}Si_{19}$ (II).

2. Experimental details

The single crystals used for the crystal structure determination of the new compounds were extracted from an ingot of composition $Ce_{9.5}Rh_{56.9}Si_{33.6}$, which had been prepared by melting the starting mixture under argon atmosphere in an arc furnace. The purity of the starting metals was better than 99%. The samples were annealed at 700 K for 720 h. Prism-like single crystals with dimensions 0.05 mm × 0.06 mm × 0.12 mm (I) and 0.07 mm × 0.09 mm × 0.13 mm (II) were examined using a CAD-4 Enraf-Nonius diffractometer (Mo Kα radiation, flat graphite monochromator).

3. Results and discussion

Experimental conditions for the X-ray single crystal investigation and results of the structure determinations are summarized in Tables 1–7. The projections of the unit cells of the $Ce_2Rh_{12}Si_7$ and $Ce_6Rh_{30}Si_{19}$ structures onto a xy-plane are shown in Figs. 1 and 2.

An interesting peculiarity of the investigated structures I and II is the presence of channels with hexagonal cross-section aligned along the c-axis. The channels are formed by Rh atoms. Inside the channels, Si atoms are located on two different sites, which are only partially occupied (see Fig. 3). As a result, the silicon content in the channels equals approximately one Si atom per unit cell.

According to the data obtained here, the crystal structure of $Ce_2Rh_{12}Si_7$ belongs to the $Ho_2Rh_{12}As_7$ structure type [3]. However, there is a difference in the position of one non-metal atom. In the structure of $Ho_2Rh_{12}As_7$, the As1 atom occupies position (0 0 0.104), whereas the Si2 and Si3 atoms in the structure of $Ce_2Rh_{12}Si_7$ occupy positions (0 0 1/4) and (0 0 0.091) (see Table 2), with a total occupancy approximately equal to the occupancy of the As1 atom.

The compound $Ce_6Rh_{30}Si_{19}$ has a structure close to those of UCo_5Si_3 [4] and $Sc_6Co_{30}Si_{19}$ [5]. $Ce_6Rh_{30}Si_{19}$ differs from UCo_5Si_3 in composition by having additional Si atoms

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Table 1
Crystallographic data and experimental conditions for the structure refinements of $Ce_2Rh_{12}Si_7$ and $Ce_6Rh_{30}Si_{19}$

	$Ce_2Rh_{12}Si_7$	$Ce_6Rh_{30}Si_{19}$
Space group	$P6_3/m$	$P6_3/m$
a (Å)	9.706(1)	15.698(2)
c (Å)	3.8394(3)	3.8571(4)
Cell volume (Å^3)	313.24(5)	823.15(17)
Z	1	1
D_{calc} (g cm^{-3})	8.924	9.006
Absorption coefficient, μ (mm^{-1})	22.97	23.35
Scan technique	$\omega/2\theta$	ω
Scan range (°)	$2.42 \leq \theta \leq 32.8$	$1.50 \leq \theta \leq 34.96$
Data collection (h, k, l)	−14/0, 0/14, 0/5	−25/0, 0/25, 0/6
Number of measured reflections	933	2810
Independent reflections	436	1349
Reflections used in refinement, $I > 2\sigma(I)$	392	1103
Number of refined parameters	27	62
$R(F)$	0.0253	0.0334
Extinction coefficient	0.0303(16)	0.00418(9)
Computer programs	SHELXS-97, SHELXL-97 [2]	

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Ce_2Rh_{12}Si_7$ (space group $P6_3/m$)

Atom	Occupancy	x	y	z	U_{eq}
Ce in 2*d*	1	2/3	1/3	1/4	0.0039(2)
Rh1 in 6*h*	1	0.06278(6)	0.44232(6)	1/4	0.00320(19)
Rh2 in 6*h*	1	0.25955(7)	0.14048(8)	1/4	0.0074(2)
Si1 in 6*h*	1	0.2903(2)	0.3966(2)	1/4	0.0035(4)
Si2 in 2*a*	0.31(4)	0	0	1/4	0.011(5)[a]
Si3 in 4*e*	0.123(8)	0	0	0.091(6)	0.002(6)[a]

[a] U_{iso}.

(Si4 and Si5) aligned along the 6_3 axes. In the $Sc_6Co_{30}Si_{19}$ structure, one of the Co atom positions is split into two positions, each with a site occupancy of ∼0.5. The resulting stoichiometry is the same as for $Ce_6Rh_{30}Si_{19}$.

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Ce_6Rh_{30}Si_{19}$ (space group $P6_3/m$)

Atom	Occupancy	x	y	z	U_{eq}
Ce in 6*h*	1	0.29585(3)	0.39654(3)	1/4	0.00561(9)
Rh1 in 6*h*	1	0.04375(4)	0.27353(4)	1/4	0.00440(11)
Rh2 in 6*h*	1	0.53684(4)	0.07531(4)	1/4	0.00440(11)
Rh3 in 6*h*	1	0.22380(4)	0.57226(4)	1/4	0.00475(11)
Rh4 in 6*h*	1	0.41620(4)	0.26385(4)	1/4	0.00437(11)
Rh5 in 6*h*	1	0.12067(4)	0.15086(5)	1/4	0.00975(13)
Si1 in 6*h*	1	0.06365(14)	0.43524(14)	1/4	0.0048(3)
Si2 in 6*h*	1	0.25359(15)	0.12196(14)	1/4	0.0042(3)
Si3 in 6*h*	1	0.55986(14)	0.24161(14)	1/4	0.0031(3)
Si4 in 2*a*	0.3(3)	0	0	1/4	0.02(2)
Si5 in 2*b*	0.2(3)	0	0	0	0.05(16)

Table 4
Anisotropic displacement parameters (Å^2) for $Ce_2Rh_{12}Si_7$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce	0.0039(2)	0.0039(2)	0.0039(3)	0	0	0.00195(12)
Rh1	0.0028(3)	0.0025(3)	0.0038(3)	0	0	0.00088(18)
Rh2	0.0056(3)	0.0158(3)	0.0042(3)	0	0	0.0079(2)
Si1	0.0035(8)	0.0021(8)	0.0048(9)	0	0	0.0012(7)

Table 5
Anisotropic displacement parameters (Å^2) for $Ce_6Rh_{30}Si_{19}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce	0.00649(18)	0.00543(17)	0.00414(14)	0	0	0.00240(14)
Rh1	0.0056(2)	0.0042(2)	0.00342(19)	0	0	0.00244(18)
Rh2	0.0049(2)	0.0051(2)	0.0041(2)	0	0	0.00316(18)
Rh3	0.0043(2)	0.0039(2)	0.0052(2)	0	0	0.00144(18)
Rh4	0.0053(2)	0.0035(2)	0.0042(2)	0	0	0.00218(18)
Rh5	0.0043(2)	0.0136(3)	0.0036(2)	0	0	−0.0013(2)
Si1	0.0047(8)	0.0040(8)	0.0049(7)	0	0	0.0017(7)
Si2	0.0061(8)	0.0035(8)	0.0028(7)	0	0	0.0025(7)
Si3	0.0033(8)	0.0032(7)	0.0016(7)	0	0	0.0008(7)
Si4	0.007(6)	0.007(6)	0.05(7)	0	0	0.003(3)
Si5	0.000(8)	0.000(8)	0.2(5)	0	0	0.000(4)

Table 6
Interatomic distances (Å) in the structure of $Ce_2Rh_{12}Si_7$

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ce	6 Rh1	3.0991(5)	Rh2	2 Si1	2.4505(13)
	6 Si1	3.1040(15)		Rh1	2.7470(9)
Rh1	Si1	2.412(2)		2 Rh1	2.8460(7)
	Si1	2.460(2)	Si1	Rh2	2.351(2)
	2 Si1	2.4771(13)		Rh1	2.412(2)
	Rh2	2.7470(9)		2 Rh2	2.4505(13)
	2 Rh1	2.7909(8)		Rh1	2.460(2)
	2 Rh2	2.8460(7)		2 Rh1	2.4771(13)
	2 Ce	3.0991(5)		2 Ce	3.1040(15)
Rh2	Si2	2.1842(7)	Si2	3 Rh2	2.1842(7)
	Si3	2.268(7)		6 Rh2	2.9079(5)
	Si1	2.351(2)	Si3	3 Rh2	2.268(6)
				3 Rh2	2.547(12)

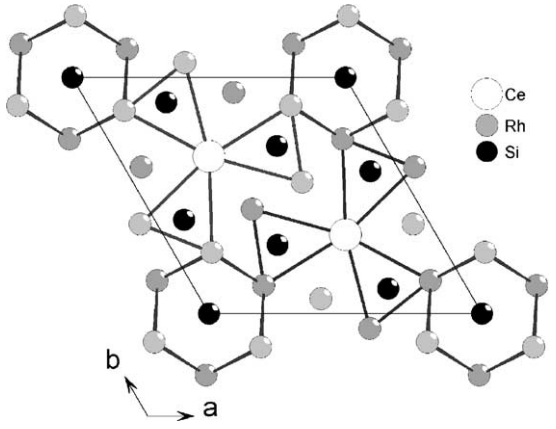

Fig. 1. Projection of one $Ce_2Rh_{12}Si_7$ unit cell onto an *xy*-plane.

Table 7
Interatomic distances (Å) in the structure of $Ce_6Rh_{30}Si_{19}$

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ce	2 Si3	3.0846(16)	Rh4	2 Rh1	2.7970(6)
	2 Si1	3.0850(15)		2 Rh3	2.8690(6)
	2 Rh4	3.0959(6)		2 Ce	3.0959(6)
	2 Rh2	3.0994(6)	Rh5	Si4	2.1703(7)
	2 Si2	3.1009(15)		Si1	2.347(2)
	2 Rh1	3.1268(6)		Si5	2.3749(7)
Rh1	Si1	2.398(2)		2 Si2	2.4642(13)
	Si2	2.436(2)		Rh1	2.7371(9)
	2 Si2	2.4804(14)		2 Rh1	2.8354(6)
	Rh5	2.7371(9)		4 Rh5	2.9034(6)
	2 Rh4	2.7970(6)	Si1	Rh3	2.3536(19)
	2 Rh5	2.8354(6)		Rh1	2.398(2)
	2 Ce	3.1268(6)		Rh2	2.414(2)
Rh2	Si1	2.414(2)		2 Rh2	2.4663(13)
	Si3	2.450(2)		2 Rh4	2.4826(13)
	2 Si1	2.4663(13)		2 Ce	3.0850(15)
	Rh4	2.7328(9)	Si2	Rh5	2.347(2)
	2 Rh2	2.8129(8)		Rh4	2.407(2)
	2 Rh3	2.8633(6)		Rh1	2.436(2)
	2 Ce	3.0994(6)		2 Rh5	2.4642(13)
Rh3	Si1	2.3536(19)		2 Rh1	2.4804(14)
	2 Si3	2.4988(13)		2 Ce	3.1009(15)
	2 Si3	2.5042(13)	Si3	Rh4	2.449(2)
	2 Rh3	2.7952(10)		Rh2	2.450(2)
	2 Rh2	2.8633(6)		2 Rh3	2.4988(13)
	2 Rh4	2.8690(6)		2 Rh3	2.5042(13)
Rh4	Si2	2.407(2)		2 Si3	2.722(3)
	Si3	2.449(2)	Si4	3 Rh5	2.1703(7)
	2 Si1	2.4826(13)		6 Rh5	2.9034(6)
	Rh2	2.7328(9)	Si5	6 Rh5	2.3749(7)

The structures of $Ho_2Rh_{12}As_7$ [3], UCo_5Si_3 [4], $Sc_6Co_{30}Si_{19}$ [5], $Zr_2Fe_{12}P_7$ [6], $Yb_6Co_{30}P_{19}$ [7], $Zr_5Co_{19}P_{12}$ [8], $U_6Co_{30}Si_{19}$ [9], $U_{10}Co_{51}Si_{33}$ [10] and the investigated structures I and II belong to a family of hexagonal structures where the short unit cell parameter $c \approx 3.7$ Å equals the height of the trigonal prisms, the coordination polyhedra formed by the transition elements and centered by As, P or Si atoms. All these structures can be considered as members of a homologous structure series (see Table 8).

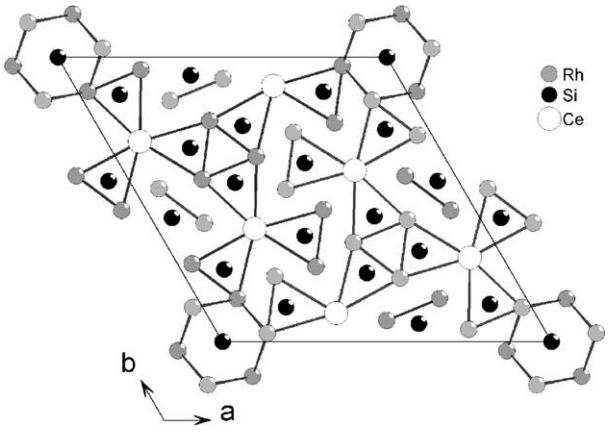

Fig. 2. Projection of one $Ce_6Rh_{30}Si_{19}$ unit cell onto an *xy*-plane.

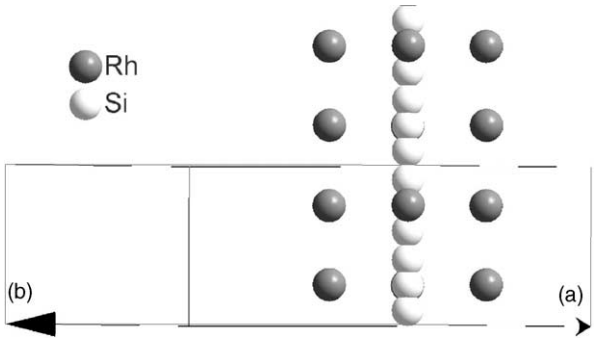

Fig. 3. Arrangement of the possible Si atom positions inside the hexagonal channels formed by Rh atoms in $Ce_2Rh_{12}Si_7$.

Table 8
Hexagonal structures with $c \approx 3.7$ Å, which belong to the structure series with general formula $R_{n(n+1)}T_{6(n^2+1)}M_{4n^2+3}$, where R is the rare earth, T the transition metal, and M the element of the IV or V main group ($n = 1$–4)

n	Compound	Cell parameters (Å)	Total number of atoms in unit cell	Reference
1	$Zr_2Fe_{12}P_7$	$a = 9.0002$, $c = 3.5920$	$Zr_2Fe_{12}P_7$	[6]
1	$Ho_2Rh_{12}As_7$	$a = 9.892$, $c = 3.859$	$Ho_2Rh_{12}As_7$	[3]
1	$Ce_2Rh_{12}Si_7$	$a = 9.706$, $c = 3.8394$	$Ce_2Rh_{12}Si_7$	This paper
2	UCo_5Si_3	$a = 14.85$, $c = 3.701$	$U_6Co_{30}Si_{18}$[a]	[4]
2	$Yb_6Co_{30}P_{19}$	$a = 14.703$, $c = 3.574$	$Yb_6Co_{30}P_{19}$	[7]
2	$Sc_6Co_{30}Si_{19}$	$a = 14.776$, $c = 3.613$	$Sc_6Co_{30}Si_{19}$	[5]
2	$Ce_6Rh_{30}Si_{19}$	$a = 15.698$, $c = 3.8571$	$Ce_6Rh_{30}Si_{19}$	This paper
3	$U_6Co_{30}Si_{19}$	$a = 21.14$, $c = 3.693$	$U_{12}Co_{60}Si_{38}$[a]	[9]
4	$U_{10}Co_{51}Si_{33}$	$a = 27.53$, $c = 3.678$	$U_{20}Co_{102}Si_{66}$[a]	[10]

[a] The content of the unit cells as estimated by the authors of [4,9,10]. Assuming one extra Si atom per unit cell, the total number of atoms in the unit cells would be $U_6Co_{30}Si_{19}$, $U_{12}Co_{60}Si_{39}$ and $U_{20}Co_{102}Si_{67}$, respectively.

In our opinion, it is possible that the hexagonal channels in the structures of UCo_5Si_3 [4], $U_6Co_{30}Si_{19}$ [9] and $U_{10}Co_{51}Si_{33}$ [10], aligned along the *c*-axis and formed by Co atoms, are also partially filled with extra Si atoms. These additional Si atoms with low occupancies were not found, probably due to the presence of a heavy element (U) and to the poor experimental facilities. Assuming one extra Si atom per unit cell in these structures, the chemical composition of the compounds would be the following: $U_6Co_{30}Si_{19}$, $U_{12}Co_{60}Si_{39}$ and $U_{20}Co_{102}Si_{67}$. Then, the general formula of this homologous series of hexagonal structures can be presented as: $R_{n(n+1)}T_{6(n^2+1)}M_{4n^2+3}$, where R is the rare earth, T the transition metal, and M the element of the IV or V main group ($n = 1 \div 4$).

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