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Crystal structure of the ternary silicide CeRh₂Si

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Abstract

The crystal structure of the compound CeRh₂Si was studied by X-ray single crystal diffraction methods and refined to $R_F = 0.038$: space group *Cmcm*, a = 4.0413(9) Å, b = 17.730(3) Å, c = 4.0675(9) Å, V = 291.45(10) Å³, Z = 4. The structure belongs to a structure type that can be considered as a site exchange variant of the known CeNiSi₂ structure type (CeSiRh₂) with slightly different axial ratios. © 2003 Elsevier B.V. All rights reserved.

Keywords: Cerium rhodium silicide; Crystal structure; CeRh2Si

1. Introduction

The ternary system Ce–Rh–Si stands out among the ternary RE–TR–M systems (RE: rare earth, TR: transition metal, M: element of the III or IV main group) due to the large number of compounds with different structure types. A new investigation of this system allowed us to establish a number of additional ternary compounds. Here, we present the structure of the new compound CeRh₂Si.

2. Experimental details

An ingot of 1 g was prepared by arc melting of a starting mixture with composition $Ce_{33}Rh_{47}Si_{20}$ under argon atmosphere. The purity of the metals was better than 99%. A homogenization annealing performed at 720 K for 700 h was followed by quenching in cold water. A needle-like single crystal with dimensions 0.03 mm × 0.03 mm × 0.12 mm was examined on a CAD4 Enraf Nonius diffractometer (Mo K α , flat graphite monochromator).

3. Results and discussion

Experimental conditions for the X-ray single crystal data collection and results of the structure determination are sum-

marized in Tables 1–4. A view of the unit cell of the CeRh₂Si structure is given in Fig. 1.

The structure of CeRh₂Si is to our knowledge the first example of a compound with composition RE1TR2M1 crystallizing in this new structure type, which can be presented as a site exchange variant of the CeNiSi₂ structure type [2] (CeSiRh₂). The structure of CeRh₂Si can be described as a combination of AlB₂- and BaAl₄-type slabs alternating along the b-axis (CeRh2 slabs with trigonal prisms and CeRh₂Si₂ slabs with tetragonal antiprisms, respectively). The structure of the previously investigated compound CeRhSi₂ [3], crystallizing with the CeNiSi₂ structure type, is built up of an alternating sequence of CeSi₂ trigonal-prism slabs and CeRh₂Si₂ tetragonal-antiprism slabs. Another example of a site exchange variant of the CeNiSi2 structure type is represented by TbFeSi₂ [4] (TbSi(FeSi)), or, more exactly, TbFe_{0.5}Si₂ [5]. The TbFe_{0.5}Si₂ type was assigned to the compounds RFeSi₂ with R = La-Nd [6] and R =Tb-Lu [5]. The structure types CeNiSi₂ and TbFe_{0.5}Si₂ are geometrically similar and all atoms are on 4c sites. The estimated position of the iron atom in TbFe_{0.5}Si₂ [5] with occupancy 0.5 is quite ambiguous as there is no atomic weight difference between a silicon atom and half an iron atom. Nevertheless, Paccard et al. [5] chose the third site (equivalent to Rh2 in Table 2) for the iron atoms, on the basis of the best final reliability factor (R = 0.063). In the CeNiSi₂ structure the transition metal atoms (Ni) are on the fourth site (equivalent to Si in Table 2).

A comparison of the atomic coordinates in CeRh₂Si and CeRhSi₂ shows a mutual exchange of the Rh and Si atom positions. This exchange causes only insignificant changes

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Table 1

Crystallographic	data	and	experimental	conditions	for	the	structure	re-
finement of CeRI	h_2Si							

Space group	Cmcm
a (Å)	4.0413(9)
<i>b</i> (Å)	17.730(3)
<i>c</i> (Å)	4.0675(9)
Cell volume (Å ³)	291.45(10)
Ζ	4
$D_{\text{calc}} (\text{g cm}^{-3})$	8.524
Absorption coefficient, μ (mm ⁻¹)	26.612
Scan technique	ω
Scan range (°)	$2.3 \le \theta \le 36.7$
Data collection h, k, l	$0 \div 6, 0 \div 28, 0 \div 6$
Independent reflections	449
Reflections used in refinement	303
$I > 2\sigma(I)$	
Number of refined parameters	17
R _F	0.0379
Computer programs	SHELXS-97, SHELXL-97 [1]

Table 2

Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for CeRh₂Si (space group *Cmcm*)

Atom	x	у	z	$U_{ m eq}$
Ce in 4c	0	0.09897(6)	1/4	0.0078(2)
Rh1 in 4c	0	0.45339(9)	1/4	0.0134(3)
Rh2 in 4c	0	0.75019(7)	1/4	0.0052(3)
Si in 4c	0	0.3203(3)	1/4	0.0057(7)

Table 3

Tuble 5					
Anisotropic	displacement	parameters	(\AA^2)	for	CeRh ₂ Si

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	<i>U</i> ₁₂
Ce	0.0084(4)	0.0099(4)	0.0051(4)	0	0	0
Rh1	0.0170(7)	0.0137(6)	0.0094(6)	0	0	0
Rh2	0.0051(5)	0.0090(5)	0.0015(5)	0	0	0
Si	0.005(2)	0.010(2)	0.002(2)	0	0	0

Table 4

Interatomic distances (Å) in the structure of CeRh₂Si

Atom1	Atom2	Distance
Ce	4 Rh1	3.0135(8)
	4 Si	3.205(2)
	2 Rh1	3.278(2)
	2 Rh2	3.3574(14)
Rh1	1 Si	2.360(5)
	2 Rh1	2.621(2)
	4 Ce	3.0135(8)
	2 Ce	3.278(2)
Rh2	2 Si	2.372(3)
	2 Si	2.387(3)
	4 Rh2	2.8669(6)
	2 Ce	3.3574(14)
	2 Ce	3.3598(14)
Si	1 Rh1	2.360(5)
	2 Rh1 2 Rh2 1 Si 2 Rh1 4 Ce 2 Ce 2 Si 2 Si 4 Rh2 2 Ce 2 Ce 2 Ce 2 Ce 1 Rh1 2 Rh2 2 Rh2	2.372(3)
	2 Rh2	2.387(3)
	4 Ce	3.205(2)



Fig. 1. A view of the unit cell of the CeRh₂Si structure: the Ce₆ trigonal prisms centered by Rh1 and the Ce₄Rh₄ tetragonal antiprisms centered by Si are emphasized.

Table 5						
Unit cell p	arameters	for the	CeRhSi ₂	[3] and	CeRh ₂ Si	structures

Structure	a (Å)	b (Å)	c (Å)	$V (\text{\AA})^3$	a:b:c
CeRhSi ₂	4.2661	16.758	4.1708	298.17	1:3.93:0.98
CeRh ₂ Si	4.0413	17.730	4.0675	291.45	1:4.39:1.01

in the interatomic distances, but an appreciable variation in the *a:b:c* ratio (see Table 5). As a result, the value of D_{calc} increases substantially, from 6.665 g cm⁻³ for CeRhSi₂ to 8.524 g cm⁻³ for CeRh₂Si. There is no solid solution between CeRh₂Si and CeRhSi₂.

According to the classification of intermetallic compounds introduced by Kripyakevich [7], the atom arrangement of CeRh₂Si can be considered as a new structure type, differing from the CeNiSi₂ type, as two essential conditions are fulfilled: (a) a noticeable change in the *a:b:c* ratio is observed, and (b) the atom distribution over the available structure sites is different.

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References

- G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Göttingen, 1997.
- [2] O.I. Bodak, E.I. Gladyshevskii, Kristallografiya 14 (1969) 990.
- [3] B. Chevalier, P. Rogl, K. Hiebl, J. Etourneau, J. Solid State Chem. 107 (1993) 327.
- [4] V.I. Yarovets, Yu.K. Gorelenko, Vestn. Lvov. Univ. Ser. Khim. 23 (1981) 20.
- [5] L. Paccard, D. Paccard, J. Allemand, J. Less-Common Met. 161 (1990) 295.
- [6] G. Venturini, B. Malaman, M. Meot-Meyer, D. Fruchart, G. Le Caer, D. Malterre, B. Roques, Rev. Chim. Miner. 23 (1986) 162.
- [7] P.I. Kripyakevich, Structure Types of Intermetallic Compounds, Nauka, Moscow, 1977.