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Crystal structure of the new ternary compound $Ce_3Ru_2In_3$

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Abstract

The crystal structure of the new ternary intermetallic compound $Ce_3Ru_2In_3$ was investigated by X-ray single crystal diffraction method. The compound crystallizes in space group *C2/m*, *mC16*, $a = 16.441(7)$ Å, $b = 4.8102(18)$ Å, $c = 4.942(3)$ Å, $\beta = 97.52(3)^\circ$, $Z = 2$ and presents a new structure type.

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Keywords: Intermetallics; Crystal structure; X-ray diffraction

1. Introduction

No systematic research was carried out up to now on interaction of the components in the ternary system Ce–Ru–In that could have led to the construction of a phase diagram or its isothermal sections. In the course of investigation of the phase equilibria in the Ce–Ru–In system at 700 °C a new ternary compound $Ce_3Ru_2In_3$ was found and its crystal structure was determined. In the present work we report the results of an X-ray single-crystal study.

2. Experimental details

Polycrystalline specimens with a total weight of about 1 g were synthesized by arc-melting of high purity metals on a water-cooled copper hearth under an argon atmosphere with zirconium getter. The samples were remelted several times to ensure their homogeneity. The mass losses after arc melting were less than 1%. The homogenization was performed in double quartz ampoule at 700 °C during 720 h. The alloys of the following compositions were prepared: $Ce_{33}Ru_{33}In_{34}$, $Ce_{30}Ru_{38}In_{32}$, $Ce_{37.5}Ru_{25}In_{37.5}$ and $Ce_{35}Ru_{29}In_{36}$. The alloys were characterized by the X-ray powder diffraction (Huber-670 image plate camera, Cu K_α radiation) and microprobe analysis (JEOL JSM 6400 scanning electron microscope equipped with a Si/Li energy dispersive analyzer). We encountered difficulties in obtaining a $Ce_3Ru_2In_3$ pure phase sample as the difference between the boiling and melting points of the components is essentially large. Nevertheless, $Ce_3Ru_2In_3$ was found as one of the phases in the four investigated alloys. From EMPA, the composition of the new phase was estimated to be $Ce_{36.7}Ru_{26.01}In_{37.29}$, in good agreement with the composition of the $Ce_3Ru_2In_3$ in atomic percent, *viz.* $Ce_{37.5}Ru_{25.0}In_{37.5}$.

A suitable plate-like single crystal was taken from the specimen prepared by melting the starting mixture of $Ce_{33}Ru_{33}In_{34}$ composition. The single crystal was first checked by Laue and rotation methods (camera RKOP, Cu radiation) to establish the suitability for X-ray intensity data collection. The intensity data were collected at room temperature with a four-circle Enraf-Nonius CAD-4 diffractometer with graphite monocromatized Mo K_α radiation. The starting atomic parameters were deduced from automatic interpretations of direct methods using SHELXS-97 [1]. The structure was refined using SHELXL-97 [2] (full-matrix least-squares on F^2) with anisotropic displacement parameters for all atoms, to $R_F = 0.053$ for 528 independent reflections with $I > 2\sigma(I)$. The experimental details are listed in Table 1. Empirical absorption correction was applied on the basis of ψ-scan data. The atomic coordinates were standardized using the program STRUCTURE TIDY [3]. The refined atomic and displacement parameters as well as interatomic distances in $Ce_3Ru_2In_3$ are listed in Tables 2 and 3.

The structure of $Ce_3Ru_2In_3$ was refined from X-ray powder data collected from the sample of $Ce_{37.5}Ru_{25}In_{37.5}$ composition using single crystal atomic parameters of $Ce_3Ru_2In_3$. The results of the Rietveld profile fitting of the $Ce_3Ru_2In_3$ (FULLPROF [4,5]) are summarized in the legend of Fig. 1. X-ray single crystal and powder data are in fine agreement.

3. Results and discussion

The $Ce_3Ru_2In_3$ compound is the first representative of a new structure type of intermetallic compounds. A projection of the

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Table 1
Experimental details

Space group	*C*2/*m*
a (Å)	16.441(7)
b (Å)	4.8102(18)
c (Å)	4.942(3)
β (°)	97.52(3)
Cell volume (Å^3)	387.4(3)
Z	2
Crystal size (mm)	0.02 × 0.06 × 0.12
D_{calc} (g cm^{-3})	8.289
Absorbtion coefficient (cm^{-1})	29.666
Scan technique	ω
Data collection *h*, *k* and *l*	$-22 \leq h \leq 22$, $0 \leq k \leq 6$ and $-6 \leq l \leq 2$
Restrictions	$I > 2\sigma(I)$
$2\theta_{max}$	59.98
Number of measured reflections	1622
Number of reflections in refinement	528
Number of refined parameters	27
R, R_w	0.053, 0.115
Goodness of fit	1.080

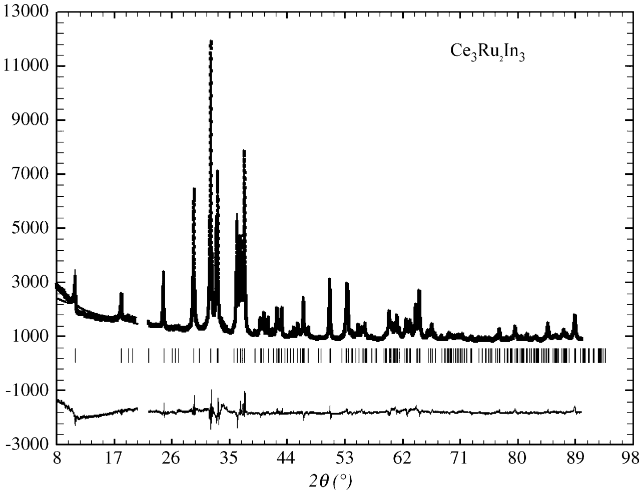

Fig. 1. Observed, calculated, and difference X-ray pattern of $Ce_3Ru_2In_3$. Details of X-ray Rietveld refinement: unit cell parameters: $a = 16.4307(3)$ Å, $b = 4.81479(7)$ Å, $c = 4.94261(9)$ Å, $\beta = 97.551(1)$°. Goodness of fit $\chi^2 = 3.82$, agreement *R*-Bragg factor $R_B = 8.80\%$, agreement *R*-structure factor $R_F = 7.32\%$, agreement value $R_{wp} = 5.80\%$ concerning weighted profile intensities, expected value from counting statistics $R_E = 2.69\%$, 205 inequivalent contributing reflections. The excluded 2θ regions contain reflections of powder substrate.

Table 3
Interatomic distances (Å) in the structure of $Ce_3Ru_2In_3$

Atom 1	Atom 2	Distance
Ce1	Ru	2.375(2)
	Ru	2.731(3)
	2Ru	3.2966(17)
	2In1	3.4758(17)
	In1	3.492(2)
	2In1	3.5392(18)
	2Ce2	3.649(2)
	2In2	3.6980(14)
	Ce2	3.735(2)
	Ce2	3.7468(19)
Ce2	4In1	3.2379(13)
	4In2	3.4481(12)
	2Ru	3.454(2)
	2Ce1	3.735(2)
	2Ce1	3.7468(19)
Ru	Ce1	2.731(3)
	Ce1	2.375(2
	2In1	2.7355(13)
	In1	2.802(2)
	2Ru	3.063(2)
	2Ce1	3.2966(17)
In1	2Ru	2.7355(13)
	Ru	2.802(2)
	2Ce2	3.2379(13)
	In2	3.246(2)
	In2	3.327(2)
	2Ce1	3.4758(17)
	Ce1	3.492(2)
	2Ce1	3.5392(18)
In2	2In1	3.246(2)
	2In1	3.327(2)
	4Ce2	3.4481(12)
	4Ce1	3.6980(10)

$Ce_3Ru_2In_3$ unit cell on the *XZ* plane and coordination polyhedra of atoms are shown in Fig. 2. The atoms in the $Ce_3Ru_2In_3$ structure form two identical layers, which lie perpendicular to [0 1 0] at heights $y = 0$ and $y = 0.5$, and are related by *a*-plane. The layers are built up of five-, four- and three-membered rings (Fig. 2).

The atoms of the smallest size, ruthenium, have a typical trigonal prismatic coordination with three additional atoms capping the lateral faces of the prism, Ru[$Ce_4Ru_2In_3$]. Whereas the In2 atoms are surrounded by a fairly distorted cuboctahedra of cerium and indium atoms, In2[Ce_8In_4], the cuboctahedra around In1 atoms formed by cerium, ruthenium, and indium

Table 2
Atomic coordinates and displacement parameters U_{ij}[a] (Å^2) of $Ce_3Ru_2In_3$

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	U_{11}	U_{22}	U_{33}	U_{13}
Ce1	4i	0.17234(7)	0	0.5733(2)	0.0130(6)	0.0123(6)	0.0063(5)	0.0012(4)
Ce2	2a	0	0	0	0.0080(7)	0.0090(7)	0.0141(7)	0.0009(5)
Ru	4i	0.21166(10)	0	0.1277(4)	0.0100(7)	0.0080(7)	0.0182(8)	0.0020(6)
In1	4i	0.63295(8)	0	0.0470(3)	0.0087(7)	0.0082(7)	0.0155(7)	0.0019(5)
In2	2d	0	0.5	0.5	0.0138(9)	0.0121(10)	0.0126(9)	0.0016(7)

[a] $U_{23} = U_{12} = 0$ for all atoms.

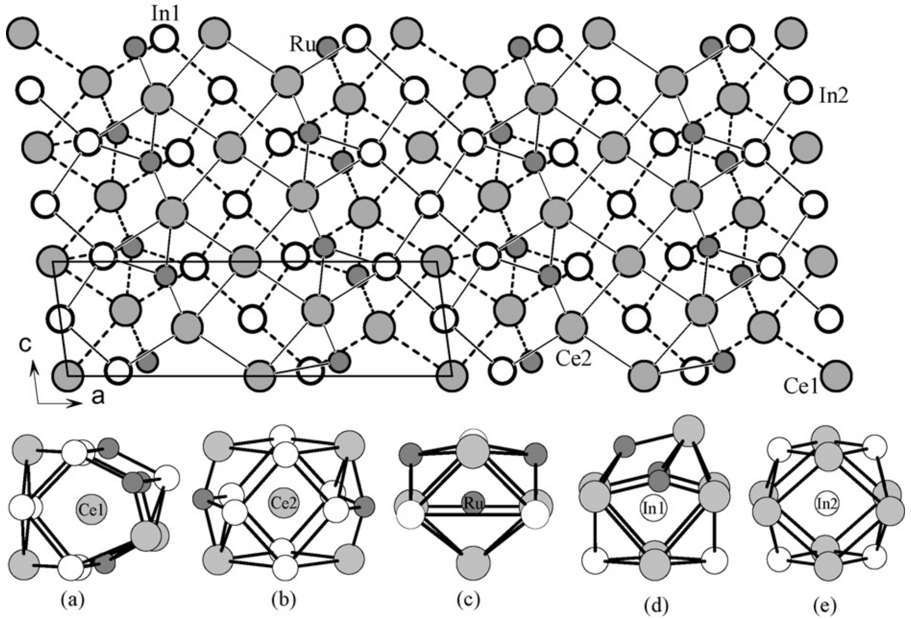

Fig. 2. Projection of the atomic layers at $y = 0.5$ (solid lines) and $y = 0$ (dotted lines) of the $Ce_3Ru_2In_3$ structure on the *XZ* plane and coordination polyhedra of Ce1(a), Ce2(b), Ru(c), In1(d), and In2(e).

atoms are severely distorted, In1[$Ce_7Ru_3In_2$]. This strong deformation of coordination polyhedra is determined mostly by a very short interatomic distance between the Ce1 and Ru atoms (2.375(2) Å), which coordinate the In1 atom. A significant difference occurs between the two crystallographically independent cerium atoms. The Ce2 atoms are surrounded by four cerium and eight indium atoms which result in a slightly distorted cuboctahedra with two additional ruthenium atoms capping the two opposite side edges of cuboctahedra Ce2[$Ce_4Ru_2In_8$]. The coordination polyhedra of the Ce1 atoms can be regarded as strongly distorted pentagonal prisms capped on all five lateral faces Ce1[$Ce_4Ru_4In_7$]. If the nearest neighbors of Ce2 atoms are at typical distances for intermetallic compounds, in the range of 3.2379–3.7468 Å, the Ce1–Ru(In, Ce) contacts cover the range from 2.375(2) to 3.7468(19) Å. Ce1 atom has one short Ce1–Ru contact (2.731(3) Å) and one very short Ce1–Ru contact (2.375(2) Å). The next nearest neighbors of Ce1 are also ruthenium atoms at the distances of 3.2966(7) Å, which correlate well with the sum of intermetallic radii of cerium and ruthenium. This peculiarity of the $Ce_3Ru_2In_3$ structure may be attributed to cerium atoms with a valence higher than 3.

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