

Crystal structure of $\text{CeRu}_{0.88}\text{In}_2$

E.V. Murashova*, A.I. Tursina, Zh.M. Kurenbaeva,
A.V. Gribanov, Yu.D. Seropegin

Department of Chemistry, Moscow State University, Moscow 119992, Russia

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Abstract

Ternary intermetallic $\text{CeRu}_{0.88}\text{In}_2$ was synthesized by arc-melting from elemental Ce, Ru, and In under an argon atmosphere. The crystal structure of $\text{CeRu}_{0.88}\text{In}_2$ was determined from single-crystal X-ray diffraction data: $a = 4.5449(11) \text{ \AA}$, $b = 10.014(2) \text{ \AA}$ and $c = 7.6854(10) \text{ \AA}$; space group $Cmcm$, $Z = 4$, MgCuAl_2 type. The structure is formed of three-dimensional framework of $[\text{Ru}_{0.88}\text{In}_2]$, in the infinite pentagonal channels of which Ce atoms are disposed. Similar to the other known ternary compounds of the Ce–Ru–In system, $\text{CeRu}_{0.88}\text{In}_2$ exhibits unusually short Ce–Ru contact equal to $2.530(4) \text{ \AA}$, which in addition is the shortest one in the row of LTIn_2 compounds with MgCuAl_2 structure type ($L = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Yb}$; $T = \text{Rh, Pd, Au}$).

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1. Introduction

Earlier no ternary compounds from Ce–Ru–In system were known [1]. A preliminary account on the crystal structure of the first representative of the Ce–Ru–In ternary intermetallics, CeRuIn_2 , has been given at a conference [2]. The crystal structure of CeRuIn_2 is isotypic with MgCuAl_2 [3] (a ternary ordered variant of the Re_3B type [4]) and demonstrates Ce–Ru contact of $2.535(5) \text{ \AA}$. Recently, a number of ternary intermetallics with new structure types were synthesized in the Ce–Ru–In system: $\text{Ce}_2\text{Ru}_2\text{In}_3$ [5], $\text{Ce}_3\text{Ru}_2\text{In}_2$ [5], $\text{Ce}_3\text{Ru}_2\text{In}_3$ [6], $\text{Ce}_{16}\text{Ru}_8\text{In}_{37}$ [7], with a remarkable common feature—very short Ce–Ru contacts in the range of $2.2345(9)$ – $2.375(2) \text{ \AA}$. The essential difference in Ce–Ru distances observed in CeRuIn_2 and in four other Ce–Ru–In compounds [5–7] may be attributed to the low-quality single-crystal of CeRuIn_2 , used in X-ray diffraction [2]. Therefore, we have decided to re-determine the crystal structure of CeRuIn_2 with the use of high-quality single-crystal.

2. Experimental

Synthesis was performed by the reaction of elemental Ce (99.8%), Ru (99.99%), and In (99.99%) in the ideal 1:1:2 atomic ratio in an arc furnace with a tungsten electrode under an argon atmosphere of $1.1 \times 10^5 \text{ Pa}$. The alloy was homogenized in an evacuated quartz ampoule by annealing in electric mufles at $700 \text{ }^\circ\text{C}$ for 700 h. The single-crystal of CeRuIn_2 found on the surface of the ingot was suitable for X-ray diffraction data collection (Enraf Nonius CAD4 diffractometer, $\text{Mo K}\alpha$, ω -scan, $\theta_{\text{max}} = 29.93^\circ$). Empirical absorption correction was applied on the basis of psi-scan data. CeRuIn_2 crystallizes in orthorhombic system with the unit cell parameters $a = 4.5449(11) \text{ \AA}$, $b = 10.014(2) \text{ \AA}$ and $c = 7.6854(10) \text{ \AA}$; space group $Cmcm$, $Z = 4$. The structure of CeRuIn_2 was solved by direct methods (SHELXS97 [8]) and refined by full-matrix least-squares procedures in the anisotropic approximation down to $R1/wR2 = 0.034/0.087$ for 276 reflections with $I > 2\sigma(I)$ and 17 refined parameters (SHELXL97 [9]).

Initial refinement assuming fully occupied Ce, Ru, and In sites led to the high value of displacement factor for Ru suggesting partial occupancy. This was verified by freeing the site occupation factor for ruthenium atom. The refined occupancy for the ruthenium site is $0.883(10)$. The exact formula of ternary intermetallic $\text{CeRu}_{0.88}\text{In}_2$ is close to the idealized composition CeRuIn_2 . The coordinates reported in Table 1 are those obtained after standardization using program STRUCTURE TIDY [10]. Selected interatomic distances are given in Table 2.

3. Results and discussion

The structure of $\text{CeRu}_{0.88}\text{In}_2$ can be presented as build of the two sorts of alternate perpendicular to $[001]$ hexagonal net-

* Corresponding author. Tel.: +7 495 9394354; fax: +7 495 9390171.
E-mail address: murashovaev@rambler.ru (E.V. Murashova).

Table 1
Atomic coordinates and displacement parameters in the structure of $\text{CeRu}_{0.88}\text{In}_2$

Atom	Wyckoff position	x/a	y/b	z/c	$U_{\text{eq}} (\text{\AA}^2)$	Occupancy
Ce	4c	0	0.43800(12)	0.25	0.0145(4)	1
In	8f	0	0.14693(10)	0.04838(12)	0.0142(3)	1
Ru	4c	0	0.6907(4)	0.25	0.0362(10)	0.883(10)

Table 2
Selected interatomic distances (\AA) in the structure of $\text{CeRu}_{0.88}\text{In}_2$

Contact	d
Ce–Ru	2.530(4)
Ce–2In	3.3010(18)
Ce–4In	3.339(2)
Ce–2Ru	3.361(3)
Ce–4In	3.4558(14)
Ce–2Ce	4.038(5)
Ru–Ce	2.530(4)
Ru–4In	2.7851(14)
Ru–2In	2.811(3)
Ru–2Ce	3.361(3)
In–2Ru	2.7851(14)
In–Ru	2.811(3)
In–In	3.035(2)
In–In	3.099(4)
In–2In	3.1588(15)
In–Ce	3.3010(18)
In–2Ce	3.339(2)
In–2Ce	3.4558(14)

works: of Ce and Ru atoms (A) (Fig. 1a), and of In atoms (B) (Fig. 1b). A-networks are plane, the interatomic distances Ce–Ru within the network are 2.530(4) and 3.361(3) \AA . B-networks are slightly corrugated (the deviation from the least-square plane is equal to 0.37 \AA). Interatomic distances In–In in B-network are 3.035(2) and 3.1588(15) \AA . The mutual arrangement of the

two networks is shown on Fig. 1c. The shortest distances Ru–In between neighbouring networks are equal to 2.7851(14) and 2.811(3) \AA (Fig. 1d).

The cerium atom is coordinated by distorted pentagonal prisms of eight indium atoms and two ruthenium atoms (Fig. 2a). Five rectangular faces of the prism are capped by two cerium atoms, two indium atoms, and one ruthenium atom. Ruthenium atom capping one of the lateral faces has the shortest distance with a central cerium atom (Ce–Ru distances 2.530(4) \AA). The ruthenium atom has a distorted trigonal prismatic coordination (2Ce + 4In) (Fig. 2b). The ruthenium prism is accomplished by one cerium atom and two indium atoms capping the rectangular faces. The indium atom is in the center of essentially distorted tetragonal prism (4Ce + 2In + 2Ru) with four additional atoms (Ce + 2In + Ru) capping the lateral faces of the prism (Fig. 2c).

The structures with common formula LTIn_2 (L = La, Ce, Pr, Nd, Sm, Eu, Gd, Yb; T = Rh, Pd, Au) of the MgCuAl_2 structure type are well described in terms of three-dimensional polyanion of composition $[\text{TIn}_2]$, inside the channels of which L atoms are displaced [11–15] (Fig. 3). In these structures interatomic distances T–In and In–In are close to the sum of the covalent radii, and distances L–T are shorter than the sum of the covalent radii independently of the kind of atoms T and L [16], that points to significant bonding between L and T atoms. Up to now, the structures of 10 indides LTIn_2 were determined and described by means of X-ray single-crystal diffraction (Table 3). Interatomic distances T–In and In–In vary insignificantly, particularly within the row Au–Pd–Rh–Ru (Table 3). The shortest

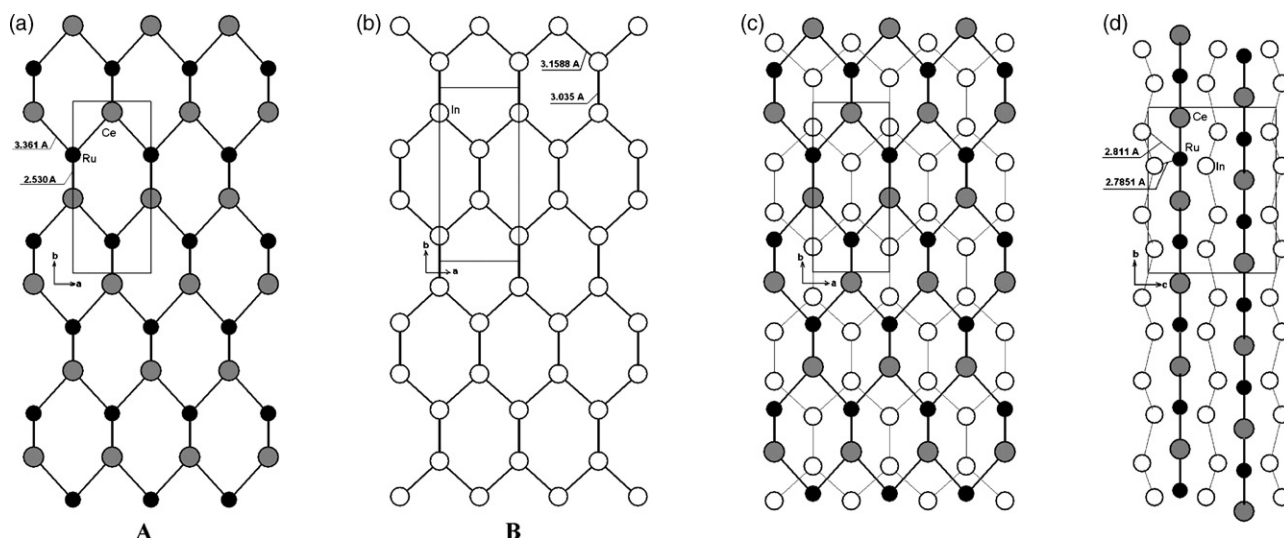


Fig. 1. Hexagonal networks A (a) and B (b). Mutual arrangement of one A and one B networks (c) viewed down the c -axis. Projection of the hexagonal networks onto (100) plane (d). Unit cell is outlined.

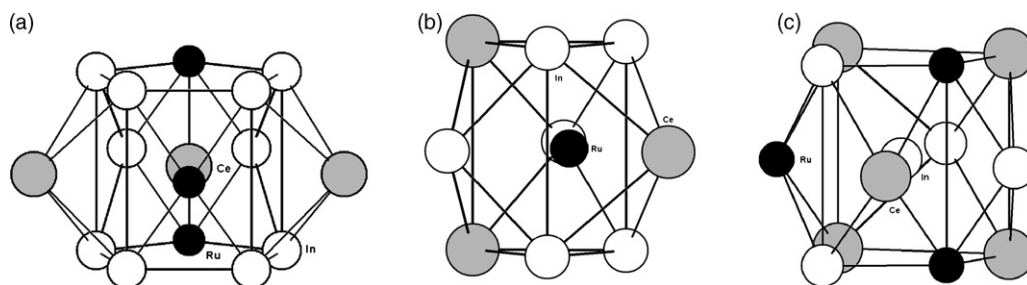


Fig. 2. Coordination polyhedra of the Ce (a), Ru (b), and In (c) atoms in the structure $\text{CeRu}_{0.88}\text{In}_2$.

Table 3
Selected interatomic distances (Å) in the structures of indides with MgCuAl_2 structure type

Compound	L–T	R(L) + R(T)	Δ (%)	T–In	In–In	Reference
EuAuIn_2	3.166	3.19	–0.8	2.838, 2.892	2.978, 3.117	[12]
YbAuIn_2	3.085	3.04	1.3	2.811, 2.850	3.007, 3.010	[15]
LaPdIn_2	3.041	2.97	2.3	2.785, 2.848	2.966, 3.094	[14]
EuPdIn_2	2.969	3.13	–5.4	2.774, 2.838	3.077, 3.236	[15]
YbPdIn_2	2.928	2.98	–1.8	2.761, 2.805	3.070, 3.084	[15]
EuRhIn_2	2.957	3.10	–4.6	2.785, 2.848	3.130, 3.184	[13]
GdRhIn_2	2.875	2.86	0.5	2.750, 2.775	3.026, 3.123	[12]
SmRhIn_2	2.840	2.91	–2.4	2.762, 2.785	3.036, 3.140	[11]
LaRhIn_2	2.822	2.94	–4.0	2.796, 2.817	3.148, 3.165	[11]
$\text{CeRu}_{0.88}\text{In}_2$	2.530	2.89	–12.5	2.785, 2.811	3.035, 3.099	This paper

distances In–In range from 2.966 to 3.148 Å and do not differ under substitution of rare earth or transition metals in various indides LTIn_2 . On the contrary, the shortest L–T distance decreases monotonously from Au to Pd and Rh and becomes very short in the ruthenium compound. The reduction of Ce–Ru distance is equal to 12.5% when compared to the sum of covalent radii of cerium and ruthenium [16]. Ce–Ru interatomic distance of 2.530(4) Å is the shortest distance in the row of compounds with MgCuAl_2 structure type, though the distances Ce–Ru in

the structures $\text{Ce}_2\text{Ru}_2\text{In}_3$, $\text{Ce}_3\text{Ru}_2\text{In}_2$, $\text{Ce}_3\text{Ru}_2\text{In}_3$, $\text{Ce}_{16}\text{Ru}_8\text{In}_{37}$ are still shorter (from 2.2345(9) to 2.375(2) Å). In all ternary structures of Ce–Ru–In system, the nearest to cerium ruthenium atom is capping one of the lateral faces of the cerium prismatic coordination polyhedron. The short distances Ce–Ru in the $\text{CeRu}_{0.88}\text{In}_2$ may be related to intermediate valance state of Ce atoms and/or to the partial occupancy of ruthenium atoms.

4. Conclusion

Similar to the other known ternary compounds of the Ce–Ru–In system, $\text{CeRu}_{0.88}\text{In}_2$ exhibits short Ce–Ru contact which is the shortest L–T interatomic distance in the row of the LTIn_2 compounds with MgCuAl_2 structure type.

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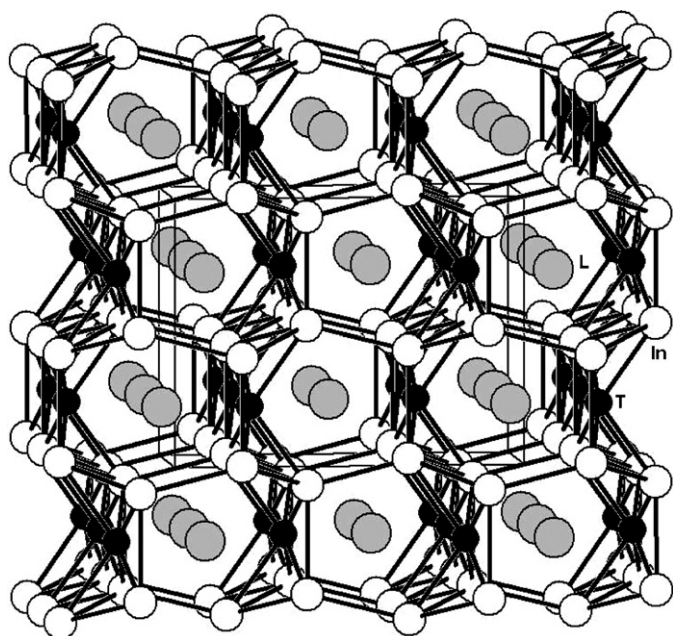


Fig. 3. Perspective view of LTIn_2 structure along [100].

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