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Crystal structure of $CeRu_{0.88}In_2$

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Abstract

Ternary intermetallic $CeRu_{0.88}In_2$ was synthesized by arc-melting from elemental Ce, Ru, and In under an argon atmosphere. The crystal structure of $CeRu_{0.88}In_2$ was determined from single-crystal X-ray diffraction data: $a = 4.5449(11)$ Å, $b = 10.014(2)$ Å and $c = 7.6854(10)$ Å; space group *Cmcm*, $Z = 4$, $MgCuAl_2$ type. The structure is formed of three-dimensional framework of $[Ru_{0.88}In_2]$, in the infinite pentagonal channels of which Ce atoms are disposed. Similar to the other known ternary compounds of the Ce–Ru–In system, $CeRu_{0.88}In_2$ exhibits unusually short Ce–Ru contact equal to 2.530(4) Å, which in addition is the shortest one in the raw of $LTIn_2$ compounds with $MgCuAl_2$ structure type (L = La, Ce, Pr, Nd, Sm, Eu, Gd, Yb; T = 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) Å. Recently, a number of ternary intermetallics with new structure types were synthesized in the Ce–Ru–In system: $Ce_2Ru_2In_3$ [5], $Ce_3Ru_2In_2$ [5], $Ce_3Ru_2In_3$ [6], $Ce_{16}Ru_8In_{37}$ [7], with a remarkable common feature—very short Ce–Ru contacts in the range of 2.2345(9)–2.375(2) Å. 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-determinate 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 1.1×10^5 Pa. The alloy was homogenized in an evacuated quartz ampoule by annealing in electric muffles at 700 °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, Mo Kα, ω-scan, $\theta_{max} = 29.93°$). Empirical absorption correction was applied on the basis of psi-scan data. $CeRuIn_2$ crystallizes in orthorhombic system with the unit cell parameters $a = 4.5449(11)$ Å, $b = 10.014(2)$ Å and $c = 7.6854(10)$ Å; 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 indide $CeRu_{0.88}In_2$ 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 $CeRu_{0.88}In_2$ can be presented as build of the two sorts of alternate perpendicular to [0 0 1] hexagonal net-

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Table 1
Atomic coordinates and displacement parameters in the structure of $CeRu_{0.88}In_2$

Atom	Wyckoff position	*x/a*	*y/b*	*z/c*	U_{eq} (Å^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 (Å) in the structure of $CeRu_{0.88}In_2$

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) Å. B-networks are slightly corrugated (the deviation from the least-square plane is equal to 0.37 Å). Interatomic distances In–In in B-network are 3.035(2) and 3.1588(15) Å. 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) Å (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) Å). 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 $[TIn_2]$, 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 raw Au–Pd–Rh–Ru (Table 3). The shortest

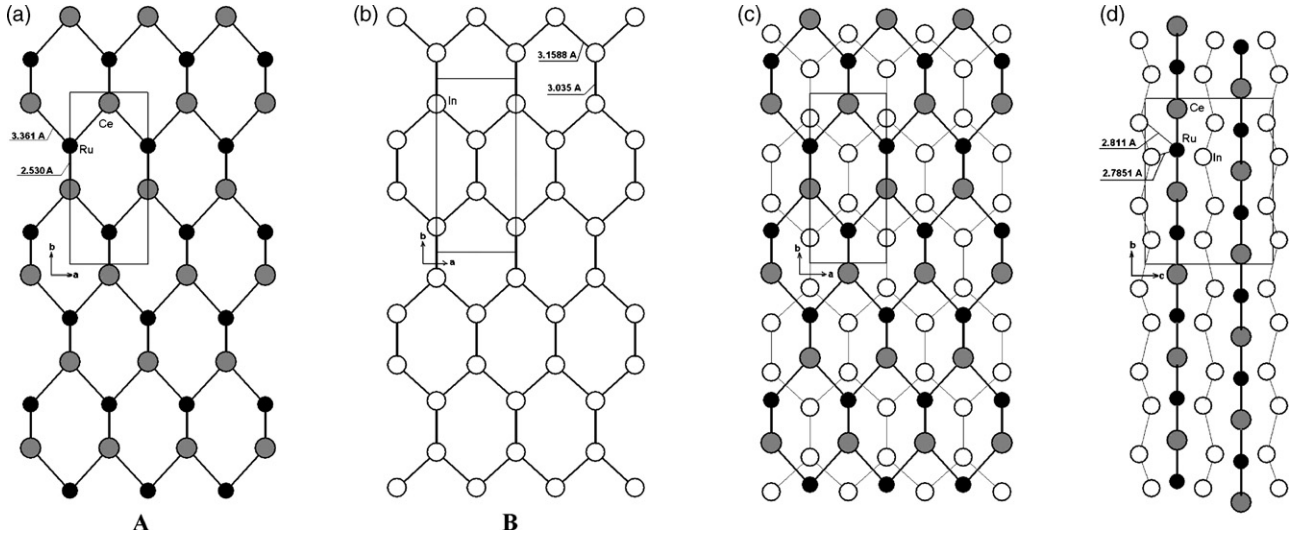

Fig. 1. Hexagonal networks A (a) and B (b). Mutual arrangement of one A and one B networks (c) viewed down the *c*-axis. Projection of the hexagonal networks onto (1 0 0) plane (d). Unit cell is outlined.