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Crystal structure of the $ThCu_5M$ (M=In, Sn) compounds

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Abstract

The structures of $ThCu_5M$, (M=In, Sn) were refined from single crystal X-ray diffraction data. Both compounds crystallize in an orthorhombic system, space group *Pnma*; $a=8.305(2)$ Å, $b=5.068(1)$ Å, $c=10.600(2)$ Å, $R1=0.0503$, 700 F^2 values for 41 variables for $ThCu_5In$; and $a=8.286(2)$ Å, $b=5.080(1)$ Å, $c=10.554(2)$ Å, $R1=0.0557$, 632 F^2 values for 41 variables for $ThCu_5Sn$. These compounds adopt the $CeCu_5Au$-type structure, an ordered variant of the $CeCu_6$-type. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Actinide compounds; Crystal structure; X-ray diffraction

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1. Introduction

Results of investigations of the crystal structure of UCu_5M (M=Al, In, Sn) compounds were recently published in Refs. [1–3]. UCu_5Al crystallizes with tetragonal symmetry and represents a new structure type. The compounds with In and Sn adopt the $CeCu_5Au$ (space group *Pnma*) [4] and $CeNi_5Sn$ (space group $P6_3/mmc$) [5] structure types, respectively. On the basis of a crystallochemical analysis of the compounds mentioned above, a relationship with simple structural types in these structures has been established. The study of their physical properties has shown a number of interesting results, a summary of which was published in Ref. [6]. For example, the powder investigation of the $U_{1-x}Th_xCu_5In$ solid solutions has proved [6] that the substitution of Th for U does not cause a change in the crystal structure. An analogous investigation [7] carried out for the tin compound led to a similar result, but in this case the Th compound was found to have a hexagonal unit cell as UCu_5Sn does. The present work reports on single crystal refinement results of the crystal structure of the $ThCu_5M$ (M=In, Sn) compounds.

2. Experimental

The specimens were obtained by arc melting compacted thorium (99.9%), copper shot (99.9999%, Johnson Matthey), indium tear drops (99.9999%, Johnson Matthey) and tin granules (>99.9%, Merck) in the desired proportion in an atmosphere of pure argon (with spongy Ti used as getter). All specimens were re-melted several times in order to obtain homogeneous alloys. The weight losses after the melting were less than 1%. The alloys were homogenized by annealing at 870 K for 1 month. All samples were stable in air and did not decompose for a long time.

X-ray phase analyses of annealed and as-cast alloys of $ThCu_5In$ and $ThCu_5Sn$ alloys indicated that they are isostructural and that their structure is similar to that of the UCu_5In compound ($CeCu_5Au$ structure type, space group *Pnma*) [2], which was investigated earlier. The X-ray powder patterns of these samples (powder diffractometer STOE, Cu Kα radiation) were indexed in an orthorhombic system and the values of the lattice parameters appeared to be close to each other. But no single crystals suitable for the crystal structure investigation have been available for these alloys. In order to obtain such single crystals, the alloys with the $ThCu_5M$ (M=Sn, In) composition weighing up to 2 g each, were put into tantalum containers and sealed in evacuated quartz ampoules. Subsequently, they were exposed to a special thermal treatment in a muffle oven. At first they were heated with a rate of 50 K per hour till 1300 K and were kept at this temperature for 3 h, then the alloys were cooled to room temperature with the rate 10 K per hour. The temperature was controlled by a CrNi–Ni thermocouple with an Eurotherm 818 thermoregulator. As a result, single crystals with irregular form

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were obtained. They were stable in air having a metallic luster and were suitable for X-ray investigations.

Quantitative and qualitative EDAX analyses, carried out by means of a Philips EDAX 515 scanning electron microscope, gave the following results, (all in atomic percentage): Th – 14.3, Cu – 70.2, In – 15.5 and Th – 12.6, Cu – 72.8, Sn – 14.6 for the single crystals containing indium and tin, respectively. These values are very close to the initial composition of the mixtures of the elemental components. No impurities have been found.

For each composition a number of single crystals were selected and tested with Laue and rotation methods (camera RKV-86, Mo K, Cu K radiation). The results of these investigations indicated for both these ternaries an orthorhombic system (Laue class – *mmm*), confirming the previous powder data, but only in the case of $ThCu_5In$. The orthorhombic form of $ThCu_5Sn$ was found for the first time. The intensities of the X-ray reflections were collected in a KUMA DIFRACTION KM-4 four-circle single crystal diffractometer equipped with a CCD camera using graphite-monochromatized Mo Kα radiation.

3. Results and discussion

For the structure refinement of $ThCu_5In$ and $ThCu_5Sn$ the atomic parameters of UCu_5In [2] were taken. The structures were subsequently refined with anisotropy displacement parameters for all atoms with SHELXL-97 [8]. Final differences in the Fourier syntheses have not revealed significant residual peaks. The results of the refinement are summarized in Table 1. Atomic coordinates and interatomic distances are listed in Tables 2 and 3.

Table 2
Atomic coordinates and isotropic displacement parameters ($Å \times 10^4$) for $ThCu_5In$ and $ThCu_5Sn$

Atom	Wyckoff site	x/a	y/b	z/c	U^*_{eq} [a]
$ThCu_5In$ (*Pnma*)					
Th	4*c*	0.2538(1)	1/4	0.5600(1)	206(3)
Cu^1	8*d*	0.0683(2)	0.5011(2)	0.3115(1)	193(4)
Cu^2	4*c*	0.0583(3)	1/4	0.1037(2)	211(5)
Cu^3	4*c*	0.3186(2)	1/4	0.2454(2)	204(5)
Cu^4	4*c*	0.4144(3)	1/4	0.0162(2)	200(5)
In	4*c*	0.1397(1)	1/4	0.8604(1)	202(4)
$ThCu_5Sn$ (*Pnma*)					
Th	4*c*	0.2530(1)	1/4	0.5579(1)	150(4)
Cu^1	8*d*	0.0699(2)	0.5020(3)	0.3116(1)	109(5)
Cu^2	4*c*	0.0638(3)	1/4	0.1029(2)	121(6)
Cu^3	4*c*	0.3195(3)	1/4	0.2460(2)	117(6)
Cu^4	4*c*	0.4159(3)	1/4	0.0174(2)	120(6)
Sn	4*c*	0.1381(2)	1/4	0.8582(1)	133(5)

[a] U^*_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

The $ThCu_5M$ (M=In and Sn) compounds crystallize with the $CeCu_5Au$-type structure, which is an ordered derivative of the $CeCu_6$-type [9]. All the crystallographic positions are (fully) occupied only by a single type of

Table 1
Crystal data and structure refinements for $ThCu_5In$ and $ThCu_5Sn$

Empirical formula	$ThCu_5In$	$ThCu_5Sn$
Formula weight	664.54	668.43
Wavelength	Mo Kα, 0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pnma* (62)	
Unit cell dimensions	$a=8.305(2)$ Å	$a=8.286(2)$ Å
	$b=5.068(1)$ Å	$b=5.080(1)$ Å
	$c=10.600(2)$ Å	$c=10.554(2)$ Å
Volume	446.2 $Å^3$	444.3 $Å^3$
Unit per cell	$Z=4$	$Z=4$
Density (calculated)	9.894 g cm^{-3}	9.994 g cm^{-3}
Absorption coefficient	61.44 mm^{-1}	62.14 mm^{-1}
$F(000)$	1136.0	1140.0
θ range for data collection	2 to 30.99°	2 to 29.41°
Index range	$-10 \le h \le 10$, $-7 \le k \le 5$, $-15 \le l \le 13$	$-11 \le h \le 11$, $-6 \le k \le 7$, $-10 \le l \le 14$
Reflection collected	2863	3547
Independent reflection	700 ($R_{int}=0.0778$)	632 ($R_{int}=0.0882$)
Reflections with $I>2\sigma(I)$	699 ($R_\sigma=0.0493$)	609 ($R_\sigma=0.0449$)
Data (restrains)parameters	700/0/41	632/0/41
Goodness-of-fit on F^2	1.186	1.166
Final R indices [$I>2\sigma(I)$]	$R1=0.0503$	$R1=0.0557$
R indices (all data)	$R1=0.0505$	$R1=0.0581$
	$wR2=0.1389$	$wR2=0.1489$
Extinction coefficient	0.00644(7)	0.00963(5)
Largest diff. peak and hole	3.24 and -3.39 e $Å^3$	5.36 and -3.71 e $Å^3$

Table 3
Interatomic distances (Å) in $ThCu_5In$ (I) and $ThCu_5Sn$ (II) (standard deviation are all equal or less than 0.003 Å)

I						II					
Th	2 Cu^4	2.931	Cu^3	2 Cu^1	2.507	Th	Cu^4	2.905	Cu^3	2 Cu^1	2.513
(C.N. = 19)	Cu^4	2.933	(C.N. = 12)	2 Cu^1	2.536	(C.N. = 19)	2 Cu^4	2.932	(C.N. = 12)	2 Cu^1	2.528
	2 Cu^2	3.012		Cu^2	2.554		2 Cu^2	2.997		Cu^2	2.577
	Cu^2	3.067		Cu^4	2.556		Cu^2	3.084		Cu^4	2.542
	2 Cu^1	3.256		Cu^2	2.632		2 Cu^1	3.263		Cu^2	2.602
	2 Cu^3	3.262		2 In	2.833		2 Cu^1	3.271		2 Sn	2.824
	2 Cu^1	3.298		2 Th	3.262		2 Cu^3	3.279		2 Th	3.279
	2 Cu^1	3.306		Th	3.378		2 Cu^1	3.303		Th	3.338
	In	3.314					Sn	3.309			
	In	3.322	Cu^4	2 Cu^1	2.514		Sn	3.311	Cu^4	2 Cu^1	2.514
	Cu^3	3.378	(C.N. = 12)	Cu^3	2.556		Cu^3	3.338	(C.N. = 12)	Cu^3	2.542
	2 In	3.418		2 Cu^1	2.567		2 Sn	3.422		2 Cu^1	2.555
				In	2.816					Sn	2.850
Cu^1	Cu^3	2.507		2 Cu^4	2.926	Cu^1	Cu^3	2.513		2 Cu^4	2.921
(C.N. = 12)	Cu^4	2.514		2 Th	2.931	(C.N. = 12)	Cu^4	2.514		2 Th	2.932
	Cu^1	2.523		Th	2.933		Cu^1	2.520		Th	2.905
	Cu^3	2.536		Cu^2	3.099		Cu^3	2.529		Cu^2	3.054
	Cu^2	2.545					Cu^2	2.548			
	Cu^1	2.545	In	Cu^2	2.666		Cu^1	2.560	Sn	Cu^2	2.656
	Cu^4	2.567	(C.N. = 14)	2 Cu^1	2.783		Cu^4	2.555	(C.N. = 14)	2 Cu^1	2.772
	In	2.783		2 Cu^1	2.810		Sn	2.772		2 Cu^1	2.787
	In	2.810		Cu^4	2.816		Sn	2.787		Cu^4	2.850
	Th	3.256		2 Cu^3	2.833		Th	3.262		2 Cu^3	2.824
	Th	3.298		2 Cu^2	3.045		Th	3.271		2 Cu^2	3.069
	Th	3.307		Th	3.314		Th	3.303		Th	3.309
				Th	3.322					Th	3.311
Cu^2	2 Cu^1	2.545		2 Th	3.418	Cu^2	2 Cu^1	2.548		2 Th	3.422
(C.N. = 11)	Cu^3	2.554				(C.N. = 11)	Cu^3	2.577			
	Cu^3	2.632					Cu^3	2.602			
	In	2.666					Sn	2.656			
	2 Th	3.012					2 Th	2.997			
	2 In	3.045					2 Sn	3.069			
	Th	3.067					Th	3.084			
	Cu^4	3.099					Cu^4	3.054			

atom. Coordination polyhedra of atoms in these structures are analogous to those in the UCu_5In structure, described in detail in a previous paper [2].

The stacking of polyhedra for the Th (19-vertices) (a) and In (Sn) (14-vertices) (b) atoms in the $ThCu_5M$ (M = In, Sn) unit cells are shown in Fig. 1. In Ref. [3] the structure of UCu_5Sn ($CeNi_5Sn$ structure type) was described as a stacking of fragments of more simple structural types, such as $CaCu_5$, $AuCu_3$ and a hypothetical structure 'T_3M'. As both the structural types of $CeNi_5Sn$ and $CeCu_5Au$ are derivatives of the $CeCu_6$-type [9], a similar description will be offered for the structures investigated here by us. In Fig. 2 are shown the stacking fragments of these types, which can be described by the following scheme:

$$2 \times ThCu_{4.5}M_{0.5} + 4 \times Cu_{1.5}M_{0.5} + 2 \times ThCu_{2.5}M_{0.5} \rightarrow Th_2Cu_9M + Cu_6M_2 + Th_2Cu_5M \rightarrow Th_4Cu_{20}M_4 \rightarrow 4 \times ThCu_5M$$

As shown in Fig. 2, these fragments are substantially deformed in comparison with the fragments characterizing the structure of UCu_5Sn. Such a deformation of the fragments may be explained by a decrease in symmetry of the crystals that we have investigated (orthorhombic, space group *Pnma*) as compared with the structure of UCu_5Sn compound (hexagonal, space group $P6_3/mmc$).

Another distinct feature of this stacking is the order of their arrangement. The stacking of fragments in the structure of the $ThCu_5M$ compounds does not proceed along one direction as in the case of the UCu_5Sn structure, but in different directions, which causes the structure to be composed mosaically (not in a linear manner). Similar types of mosaic and not linear stackings are, for example, formed by fragments of the simple CsCl and AlB_2 structure types. This is observed in other structures, such as in the R_2Ni_2In (Mn_2AlB_2 structure type, space group *Cmmm*) as well as in R_2Cu_2In and $R_2Ni_{2-x}In$ (Mo_2FeB_2 structure type, space group *P4/mbm*) [10,11]. The mosaic

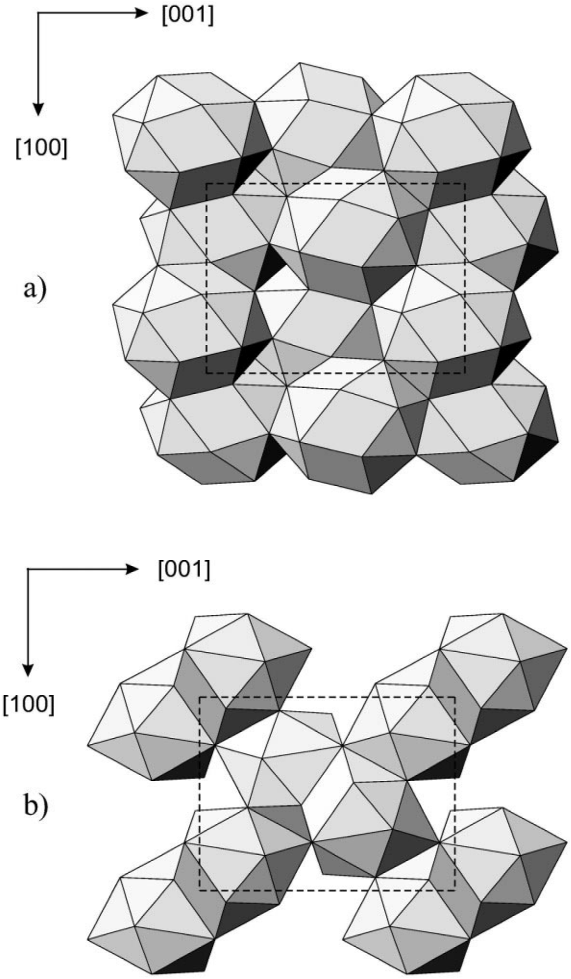

Fig. 1. The arrangement of the polyhedra for the Th (19-vertices) (a) and In (Sn) (14-vertices) (b) atoms in the $ThCu_5M$ structures.

stacking of the fragments of the simple $CaCu_5$, $AuCu_3$ and the hypothetical 'M_3X' types can be also seen in the $CeCu_{4.38}In_{1.62}$ (space group *Pnnm*) compound [12] (Fig. 3), the structure of which is a derivative of the $CeCu_6$-type (one of the lattice parameters is doubled compared to that in the prototype $CeCu_5Au$ structure).

The analysis of interatomic distances in the compounds investigated by us indicates the absence of a significant reduction in lengths of the contacts when compared to the sum of the atomic radii of the composed elements. The values of reduction are expressed by $\delta = (1 - d/[r_1 + r_2]) \times 100\%$, where d is interatomic distance (Å) and r_1 and r_2 the atomic radii of elements (Å). The largest δ values are observed for the following distances: Cu(2)–In, $\delta = 2.666$ Å (9.3%) and Cu(2)–Sn, $\delta = 2.656$ Å (7.1%). The reduction of interatomic distances for the other atoms in these structures is rather insignificant and the values of d do not exceed 5%.

The still open question not solved is the polymorphism of the $ThCu_5Sn$ compound, which we hope to solve in our further single crystal refinements when crystals will become available.

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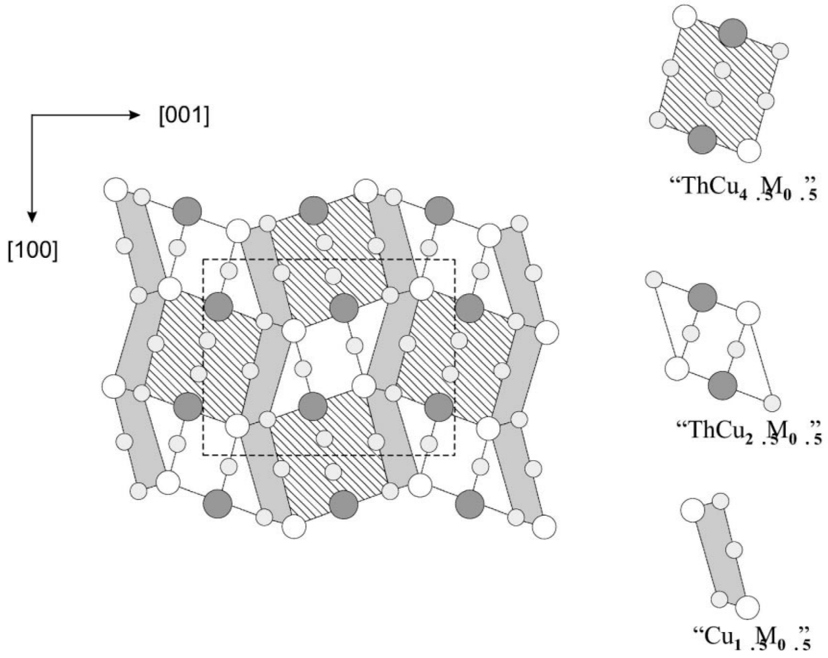
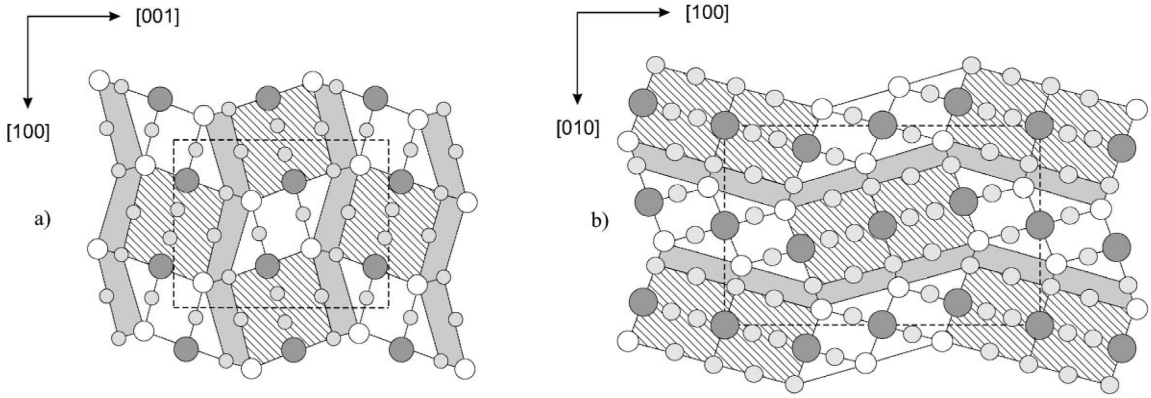


Fig. 2. The stacking of the fragments of similar types $CaCu_5$, $AuCu_3$ and a hypothetical structure 'T_3M' in the $ThCu_5M$ structures (its projection is shown as dashed lines).



$ThCu_5M$ ($CeCu_5Au$-type, sp. gr. *Pnma*) $RCu_{4.38}In_{1.62}$ ($CeCu_{4.38}In_{1.62}$-type, sp. gr. *Pnnm*)

Fig. 3. The mosaic stacking of the fragments in the $CeCu_5Au$ and $CeCu_{4.38}In_{1.62}$ types.

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