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On the crystal structure of the "cage"-like aluminide URu_3Al_{10}

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The novel ternary aluminide URu_3Al_{10} crystallizes in the orthorhombic (*Imma* space group) $CeRu_3Al_{10}$ structure type with cell parameters *a* = 4.1925(1) Å, *b* = 12.4173(5) Å and *c* = 17.5328(6) Å. The combination of (i) short Al-Al and Ru-Al interatomic distances and (ii) long U-Al and U-Ru distances classifies this intermetallic phase as a "cage"-like one, similarly to other Al-rich U-*T*-Al (*T* = transition metal) compounds.

Uranium aluminide / Cage-like compound / Single crystal X-ray diffraction

Introduction

Cage-like compounds have attracted strong interest in the last years due to their potential industrial applications in diverse fields such as gas storage or controlled molecule delivery, but also for their intriguing physical properties. Among *f*-element based intermetallic compounds, the skutterudites are intensively investigated due to their rather "high" superconducting transitions (*e.g.* 7.2 K for $LaRu_4P_{12}$ [1] or 8.3 K for $PrPt_4Ge_{12}$ [2]) and rattling-atom enhanced thermoelectric properties (*e.g.* $ZT = 1.1$ at 873 K for $CeFe_4Sb_{12}$ [3]). One can also cite the RT_2X_{20} compounds (*R* = rare earth, *T* = transition metal and *X* = Al, Zn) with cubic $CeCr_2Al_{20}$-type structure, where superconductivity is reported for RT_2Zn_{20} (*R* = La, Pr; *T* = Ru, Ir) [4] and MV_2Al_{20} (*M* = Sc, Lu, Y) [5].

In the U–*T*–Al ternary systems, cage-like compounds are reported to form for high Al-concentrations with different structure types depending on the electronic configuration of the transition metal. For *T* = Ti, col. VB, col. VIB, and Mn, the Al-richest phase reported is UT_2Al_{20}, crystallizing in the above mentioned cubic $CeCr_2Al_{20}$-type, and mostly presenting enhanced Pauli paramagnetic behavior [6-9], but in the case of *T* = Mn it orders ferromagnetically below $T_C = 20$ K [10] due to the Mn network [11]. For *T* = col. VB and col. VIB elements, another phase with formula $U_6T_4Al_{43}$ and hexagonal $Ho_6Mo_4Al_{43}$ structure type forms [12,13] where a U-U dimer is enclosed in a $[T_2Al_{24}]$ peanut-like cage [14]. Multi-step magnetic ordering resulting from a competition between intra- and inter- U-U dimer interaction has been reported in the case of *T* = Nb [9]. For *T* = Fe, Ru, Os, UT_2Al_{10} forms with the orthorhombic $YbFe_2Al_{10}$ structure type [15-17]. The physical properties are dominated by fluctuation phenomena, as evidenced by magnetic and (magneto)electrical measurements both on poly- and single-crystalline samples [15-18].

Within our investigation of the U–Ru–Al system, we have evidenced the existence of a novel ternary phase with composition URu_3Al_{10} and $CeRu_3Al_{10}$ structure type [19] that can be described as a cage-like compound. This article will describe the crystal structure of this ternary uranium aluminide determined by single crystal X-ray diffraction.

Experimental

The samples were prepared by arc-melting of the elemental components (purity: U-3N, Ru-4N and Al-5N), and re-melted several times to ensure homogeneity. Then, the samples were placed in a water-cooled copper crucible and annealed for 4 h at 1473 K in a high-frequency induction furnace, in order to homogenize the composition and increase the average crystal size.

The samples were characterized by powder X-ray diffraction (XRD) (Bruker D8 Advance θ-2θ diffractometer, Cu Kα_1 radiation, $\lambda = 1.5406$ Å) and scanning electron microscopy (SEM) (JEOL 6400 JSM microscope) coupled to energy-dispersive spectroscopy (EDS) (Oxford Link Isis spectrometer).

Small single crystals suitable for XRD experiments were collected from a crushed annealed sample. The diffraction intensities were collected at room temperature on a Nonius Kappa CCD four-circle diffractometer working with Mo $K\alpha$ radiation (λ = 0.71073 Å). The integration and reduction of redundant reflections of the different data sets as well as the cell refinements were performed using the SADABS software [20]. Structural models were determined by direct methods using SIR-97 [21]. All the structure refinements and Fourier syntheses were made with the help of SHELXL-97 [22]. The atomic positions have been standardized using STRUCTURE TIDY [23]. The Diamond 2.1b software was used to represent the crystal structure [24].

Results and discussion

A ternary phase with chemical composition 7U-21Ru-72Al (in at.%) was observed in as-cast samples with close initial composition. In order to characterize it, samples were prepared with this 7-21-72 composition. These showed the presence of the new phase, but also of URu_2Al_{10}, UAl_3 and $RuAl_2$, suggesting peritectic formation of the "URu_3Al_{10}" phase. Annealing at 1473 K for 4 h in an induction furnace resulted in an increase of the relative quantity of the targeted phase, but not in a pure sample. Long-term annealing (1 week or more) at 1173 K or lower temperature results in the disappearance of the phase, suggesting its eutectoid decomposition above this temperature. Powder XRD patterns of the new aluminide were well indexed by considering an orthorhombic (*Imma*, no. 74) $CeRu_3Al_{10}$-type structure [19], in addition to the impurity phase patterns.

The reported half occupancies of the Al1 (8*h*) and Al3 (8*h*) positions, as well as the mixed Ru/Al occupancy of a 4*e* site in the cerium-based compound, motivated us to further characterize the crystal structure of the uranium-based aluminide using single crystal XRD. Small single crystals were picked up from the annealed sample and used for XRD experiments. The diffraction peaks were well indexed in an orthorhombic cell with parameters a = 4.1925(1) Å, b = 12.4173(5) Å and c = 17.5328(6) Å and the reflection conditions were compatible with the expected *Imma* space group.

The results of the crystal structure solution and refinements are summarized in Table 1, while the standardized atomic positions are gathered in Table 2. The atomic distribution on 10 independent Wyckoff position in URu_3Al_{10} perfectly fits that of the cerium-based isostructural phase, confirming the structure type of our intermetallics.

Table 1 Data collection and structure refinement for URu_3Al_{10}.

Empirical formula	URu_3Al_{10}
Formula weight (g mol^{-1})	811.04
Structure type	$CeRu_3Al_{10}$
Space group	*Imma* (no. 74)
Unit cell parameters (Å)	a = 4.1925(1) b = 12.4173(5) c = 17.5328(6)
Unit cell volume (Å^3)	912.75(5)
Z / calculated density (g cm^{-3})	4 / 5.902
Absorption coefficient (mm^{-1})	23.450
Crystal color and habit	metallic luster, prism
Crystal size (μm×μm×μm)	87×38×17
Theta range (°)	3.85 to 41.99
Limiting indices	$-4 \le h \le 7$ $-22 \le k \le 23$ $-29 \le l \le 32$
Collected / unique reflections	10021 / 1803
Absorption correction	Semi-empirical
R(int)	0.0458
Data / restraints / parameters	1803 / 0 / 55
Goodness of fit on F^2	1.085
R indices [$I > 2\sigma(I)$]	$R1$ = 0.0283 $wR2$ = 0.0403
Extinction coefficient	0.00079(5)
Largest difference peak and hole (e Å^{-3})	2.142 / -2.440

Table 2 Refined atomic positions, occupancies and equivalent displacement parameters.

Atom	Wyckoff position	*x*	*y*	*z*	Occupancy	U_{eq} (10^3 Å²)
U1	4*e*	0	¼	0.9653(1)	1	6(1)
Ru1	8*h*	0	0.0551(1)	0.1339(1)	1	4(1)
Ru2	4*e*	0	¼	0.6846(1)	1	6(1)
Al1	8*h*	0	0.0445(2)	0.2836(2)	0.492(6)	8(1)
Al2	8*h*	0	0.0808(1)	0.6009(1)	1	12(1)
Al3	8*h*	0	0.1206(2)	0.2844(2)	0.508(6)	11(1)
Al4	8*h*	0	0.1358(1)	0.4352(1)	1	8(1)
Al5	8*h*	0	0.6334(1)	0.1950(1)	1	7(1)
Al6	4*e*	0	¼	0.1528(1)	1	10(1)
Al7	4*a*	0	0	0	1	8(1)

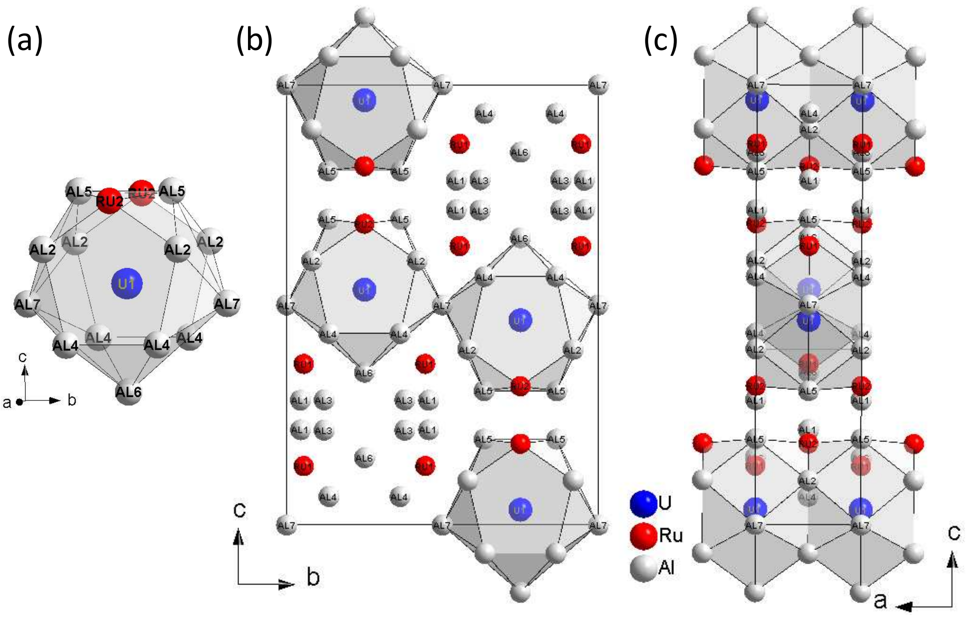

Fig. 1 (a) “Cage”-like uranium coordination sphere in the orthorhombic URu_3Al_{10} structure and view of the structure along (b) the *a*-axis and (c) the *b*-axis.

The 8*h* sites occupied by Al1 and Al3 are much too close (0.945(4) Å) to be occupied simultaneously. Their occupancies were first refined independently, leading to occupancies of 0.49 for Al1 and 0.51 for Al3. Further refinements were performed constraining the sum of the occupancies to 1, leading to a final Al1/Al3 distribution of 0.492(6)/0.508(6), very close to a perfect half occupancy of these sites. Similarly to $CeRu_3Al_{10}$, no diffraction feature that could correlate this half occupancy to any ordered superstructure, in particular to the monoclinic $U_2Co_6Al_{19}$-type [25], was found. In order to rule out the possibility of Ru/Al substitution on the other sites, their occupancies were refined one by one. None of them showed any significant deviation from full occupancy, including the Ru2 4*e* site that accepts 17 at.% Al in the cerium-based compound. The crystallographic composition is thus exactly URu_3Al_{10}, in perfect agreement with the SEM-EDS analyses.

With the exception of the unphysical shortest Al1-Al3 distance that leads to half occupancy of these sites, all the other Ru-Ru, Ru-Al and Al-Al interatomic distances (Table 3) correspond well to those encountered in the other ternary U–Ru–Al aluminides [26] and are slightly shorter than the sum of the metallic radii of the elements (r_{Ru} = 1.339 Å and r_{Al} = 1.432 Å [27]), evidencing strong bonding between these elements.

The coordination sphere around the uranium atoms (Fig. 1a), made of 13 Al- and 2 Ru-atoms, exhibits a slightly different behavior with all U-ligand distances being significantly larger than the sum of the metallic

Table 3 Selected interatomic distances.

Atom	Ligand	Distance (Å)	Atom	Ligand	Distance (Å)
U1	4 Al4	3.074(1)	Al3	2 Al3 / 2 Al1	2.419(3) / 2.590(2)
	2 Al5	3.161(2)		1 Al4	2.651(3)
	2 Al7	3.1634(2)		2 Ru1	2.666(2)
	4 Al2	3.186(2)		1 Ru1	2.761(3)
	1 Al6	3.287(1)		1 Al6	2.812(3)
	2 Ru2	3.361(1)		2 Al6	2.862(2)
				1 Al2	3.209(3)
Ru1	1 Al6	2.4432(4)			
	1 Al7	2.4457(3)	Al4	2 Ru1	2.6210(8)
	2 Al1 / 2 Al3	2.550(2) / 2.666(2)		1 Al3 / 1 Al1	2.651(3) / 2.890(3)
	1 Al5	2.573(2)		1 Al2	2.763(2)
	2 Al4	2.6210(8)		1 Al4	2.837(3)
	1 Al1 / 1 Al3	2.627(3) / 2.761(3)		2 Al7	2.9198(9)
	2 Al2	2.753(1)		2 Al6	2.965(2)
				1 Al2	2.983(2)
Ru2	4 Al5	2.5544(8)		1 U1	3.0737(9)
	2 Al5	2.560(2)			
	2 Al2	2.562(2)	Al5	2 Ru2	2.5544(8)
	2 Ru2	3.1070(6)		1 Ru2	2.560(2)
	2 U1	3.3617(4)		1 Ru1	2.573(2)
				1 Al1 / 1 Al3	2.700(3) / 3.522(3)
Al1	2 Al1 / 2 Al3	2.405(3) / 2.590(2)		2 Al2	2.746(2)
	2 Ru1	2.550(2)		2 Al5	2.849(2)
	1 Al2	2.554(3)		1 Al5	2.896(3)
	1 Ru1	2.627(3)		1 Al1 / 1 Al3	3.068(3) / 3.804(3)
	1 Al5	2.700(3)		1 U1	3.161(2)
	1 Al4	2.890(3)			
	2 Al5	3.068(3)	Al6	2 Ru1	2.4432(4)
				2 Al3 / 2 Al1	2.812(3) / 3.431(3)
Al2	1 Al1 / 1 Al3	2.554(3) / 3.209(3)		4 Al3 / 4 Al1	2.862(2) / 3.486(3)
	1 Ru2	2.562(1)		4 Al4	2.965(2)
	2 Al5	2.746(2)		1 U1	3.287(1)
	2 Ru1	2.753(1)			
	1 Al4	2.763(2)	Al7	2 Ru1	2.4457(3)
	2 Al7	2.921(1)		4 Al4	2.9198(9)
	1 Al4	2.983(2)		4 Al2	2.921(1)
	2 U1	3.186(2)		2 U1	3.1634(2)

radii of the elements (r_U = 1.56 Å) and slightly larger than the 2.9-3.0 Å distances encountered in *e.g.* the UAl_x (x = 3, 4) binaries, URuAl [26], or $U_3Ru_4Al_{12}$ [28]. Similarly to URu_2Al_{10}, the new compound can thus be classified as a “cage”-like material. In the URu_3Al_{10} structure, the cages around the uranium atoms are connected *via* U7 atoms along the *b*-axis (Fig. 1b) and share their pentagonal faces along the *a*-axis (Fig. 1c), forming 2D layers parallel to the (*a*,*b*) plane of the orthorhombic cell.

According to the various physical properties of the cage-like uranium aluminides described in the introduction, further efforts will be made to improve the purity of the samples for magnetic and electrical measurements.

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