

## On the crystal structure of the “cage”-like aluminide URu<sub>3</sub>Al<sub>10</sub>

Mathieu PASTUREL<sup>1\*</sup>, Konrad WOCHOWSKI<sup>2</sup>, Henri NOËL<sup>1</sup>

<sup>1</sup> Institut des Sciences Chimiques de Rennes, Chimie du Solide et Matériaux, UMR CNRS 6226, Université Rennes 1, Campus de Beaulieu, bât. 10A, 263 av. Général Leclerc, 35042 Rennes Cedex, France

<sup>2</sup> Institute of Low Temperature and Structural Research, Polish Academy of Sciences, ul. Okólna 2, 50-422 Wrocław, Poland

\* Corresponding author. Tel.: +33-2-23-23-58-61; e-mail: mathieu.pasturel@univ-rennes1.fr

Received November 30, 2016; accepted December 28, 2016; available on-line August 14, 2017

The novel ternary aluminide URu<sub>3</sub>Al<sub>10</sub> crystallizes in the orthorhombic (*Imma* space group) CeRu<sub>3</sub>Al<sub>10</sub> 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<sub>4</sub>P<sub>12</sub> [1] or 8.3 K for PrPt<sub>4</sub>Ge<sub>12</sub> [2]) and rattling-atom enhanced thermoelectric properties (*e.g.*  $ZT = 1.1$  at 873 K for CeFe<sub>4</sub>Sb<sub>12</sub> [3]). One can also cite the  $RT_2X_{20}$  compounds ( $R$  = rare earth,  $T$  = transition metal and  $X$  = Al, Zn) with cubic CeCr<sub>2</sub>Al<sub>20</sub>-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<sub>2</sub>Al<sub>20</sub>-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<sub>2</sub>Al<sub>10</sub> 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<sub>3</sub>Al<sub>10</sub> and CeRu<sub>3</sub>Al<sub>10</sub> 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  $\theta$ - $2\theta$  diffractometer, Cu  $K\alpha_1$  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 ( $\lambda = 0.71073 \text{ \AA}$ ). 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<sub>2</sub>Al<sub>10</sub>, UAl<sub>3</sub> and RuAl<sub>2</sub>, suggesting peritectic formation of the “URu<sub>3</sub>Al<sub>10</sub>” 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<sub>3</sub>Al<sub>10</sub>-type structure [19], in addition to the impurity phase patterns.

The reported half occupancies of the Al1 (*8h*) and Al3 (*8h*) positions, as well as the mixed Ru/Al occupancy of a *4e* 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  $a = 4.1925(1) \text{ \AA}$ ,  $b = 12.4173(5) \text{ \AA}$  and  $c = 17.5328(6) \text{ \AA}$  and the reflection conditions were compatible with the expected *Imma* space group.

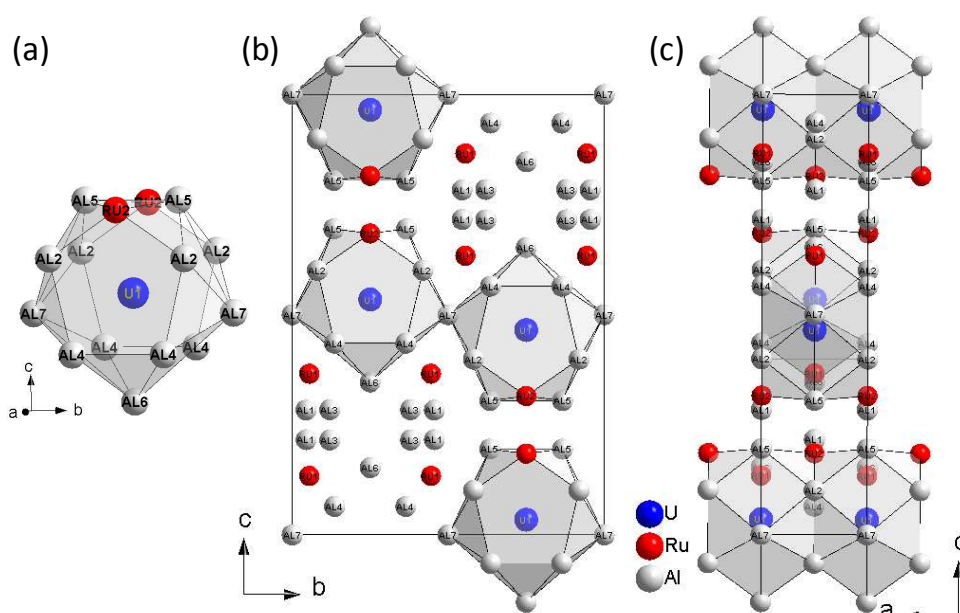
The results of the crystal structure solution and refinements are summarized in Table 1, while the standardized atomic positions are gathered in Table 2. The atomic distribution on 10 independent Wyckoff position in URu<sub>3</sub>Al<sub>10</sub> perfectly fits that of the cerium-based isostructural phase, confirming the structure type of our intermetallics.

**Table 1** Data collection and structure refinement for URu<sub>3</sub>Al<sub>10</sub>.

Empirical formula	URu <sub>3</sub> Al <sub>10</sub>
Formula weight (g mol <sup>-1</sup> )	811.04
Structure type	CeRu <sub>3</sub> Al <sub>10</sub>
Space group	<i>Imma</i> (no. 74)
Unit cell parameters (Å)	$a = 4.1925(1)$ $b = 12.4173(5)$ $c = 17.5328(6)$
Unit cell volume (Å <sup>3</sup> )	912.75(5)
Z / calculated density (g cm <sup>-3</sup> )	4 / 5.902
Absorption coefficient (mm <sup>-1</sup> )	23.450
Crystal color and habit	metallic luster, prism
Crystal size ( $\mu\text{m} \times \mu\text{m} \times \mu\text{m}$ )	87 $\times$ 38 $\times$ 17
Theta range (°)	3.85 to 41.99
Limiting indices	$-4 \leq h \leq 7$ $-22 \leq k \leq 23$ $-29 \leq l \leq 32$
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 <sup>-3</sup> )	2.142 / -2.440

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

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> <sub>eq</sub> (10 <sup>3</sup> Å <sup>2</sup> )
U1	4 <i>e</i>	0	¼	0.9653(1)	1	6(1)
Ru1	8 <i>h</i>	0	0.0551(1)	0.1339(1)	1	4(1)
Ru2	4 <i>e</i>	0	¼	0.6846(1)	1	6(1)
Al1	8 <i>h</i>	0	0.0445(2)	0.2836(2)	0.492(6)	8(1)
Al2	8 <i>h</i>	0	0.0808(1)	0.6009(1)	1	12(1)
Al3	8 <i>h</i>	0	0.1206(2)	0.2844(2)	0.508(6)	11(1)
Al4	8 <i>h</i>	0	0.1358(1)	0.4352(1)	1	8(1)
Al5	8 <i>h</i>	0	0.6334(1)	0.1950(1)	1	7(1)
Al6	4 <i>e</i>	0	¼	0.1528(1)	1	10(1)
Al7	4 <i>a</i>	0	0	0	1	8(1)

**Fig. 1** (a) “Cage”-like uranium coordination sphere in the orthorhombic URu<sub>3</sub>Al<sub>10</sub> 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<sub>3</sub>Al<sub>10</sub>, no diffraction feature that could correlate this half occupancy to any ordered superstructure, in particular to the monoclinic U<sub>2</sub>Co<sub>6</sub>Al<sub>19</sub>-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<sub>3</sub>Al<sub>10</sub>, 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 ( $r_{\text{Ru}} = 1.339$  Å and  $r_{\text{Al}} = 1.432$  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)	
Ru1	1 Al6	2.4432(4)	Al4	1 Al2	3.209(3)	
	1 Al7	2.4457(3)		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)	
Ru2	4 Al5	2.5544(8)	Al2	1 Al2	2.983(2)	
	2 Al5	2.560(2)		1 U1	3.0737(9)	
	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)
Al1	2 Al1 / 2 Al3	2.405(3) / 2.590(2)	1 Al1 / 1 Al3		2.700(3) / 3.522(3)	
	2 Ru1	2.550(2)	2 Al2		2.746(2)	
	1 Al2	2.554(3)	2 Al5	2.849(2)		
	1 Ru1	2.627(3)	1 Al5	2.896(3)		
	1 Al5	2.700(3)	1 Al1 / 1 Al3	3.068(3) / 3.804(3)		
	1 Al4	2.890(3)	1 U1	3.161(2)		
	2 Al5	3.068(3)	Al6	2 Ru1	2.4432(4)	
Al2	1 Al1 / 1 Al3	2.554(3) / 3.209(3)		2 Al3 / 2 Al1	2.812(3) / 3.431(3)	
	1 Ru2	2.562(1)		4 Al3 / 4 Al1	2.862(2) / 3.486(3)	
	2 Al5	2.746(2)		4 Al4	2.965(2)	
	2 Ru1	2.753(1)		1 U1	3.287(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 ( $r_U = 1.56 \text{ \AA}$ ) and slightly larger than the 2.9-3.0 Å distances encountered in *e.g.* the UAl<sub>x</sub> ( $x = 3, 4$ ) binaries, URuAl [26], or U<sub>3</sub>Ru<sub>4</sub>Al<sub>12</sub> [28]. Similarly to URu<sub>2</sub>Al<sub>10</sub>, the new compound can thus be classified as a “cage”-like material. In the URu<sub>3</sub>Al<sub>10</sub> 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.

### Acknowledgements

This work was supported by the “FINUG” CNRS-PAN PICS Project in the period 2015-2017.

### References

- [1] G.P. Meisner, *Physica B&C* 108 (1981) 763-764.
- [2] R. Gumenuik, W. Schnelle, H. Rosner, M. Niklas, A. Leithe-Jasper, Y. Grin, *Phys. Rev. Lett.* 100 (2008) 017002.
- [3] D.T. Morelli, G.P. Meisner, *J. Appl. Phys.* 77 (1995) 3777-3781.
- [4] T. Onimaru, K.T. Matsumoto, Y.F. Inoue, K. Umeo, Y. Saiga, Y. Matsushita, R. Tamura,

- K. Nishimoto, I. Ishii, T. Suzuki, T. Takabatake, *J. Phys. Soc. Jpn.* 79 (2010) 033704.
- [5] M.J. Winiarski, B. Wiendlocha, M. Sternik, P. Wisniewski, J.R. O'Brien, D. Kaczorowski, T. Klimczuk, *Phys. Rev. B* 93 (2016) 134507.
- [6] I. Halevy, E. Sterer, M. Aizenshtein, G. Kimmel, D. Regev, E. Yahel, L.C.J. Pereira, A.P. Gonçalves, *J. Alloys Compd.* 319 (2001) 19-21.
- [7] P. Swatek, D. Kaczorowski, *J. Solid State Chem.* 191 (2012) 191-194.
- [8] Y. Matsumoto, T.D. Matsuda, N. Tateiwa, E. Yamamoto, Y. Haga, Z. Fisk, *J. Kor. Phys. Soc.* 63 (2013) 363-366.
- [9] C. Moussa, A. Berche, M. Pasturel, J. Barbosa, B. Stepnik, S. Dubois, O. Tougait, *J. Alloys Compd.* 691 (2017) 893-905.
- [10] C.H. Wang, J.M. Lawrence, E.D. Bauer, K. Kothapalli, J.S. Gardner, F. Ronning, K. Gofryk, J.D. Thompson, H. Nakotte, F. Trouw, *Phys. Rev. B* 82 (2010) 094406.
- [11] P. Wisniewski, P. Swatek, A. Gukasov, D. Kaczorowski, *Phys. Rev. B* 86 (2012) 054438.
- [12] S. Niemann, W. Jeitschko, *Z. Metallkd.* 85 (1994) 345-349.
- [13] S. Niemann, W. Jeitschko, *J. Solid State Chem.* 116 (1995) 131-135.
- [14] K. Fushiya, R. Miyazaki, R. Higashinaka, T.D. Matsuda, Y. Aoki, *JPS Conf. Proc.* 3 (2014) 011018.
- [15] T. Sugai, Y. Haga, T.D. Matsuda, E. Yamamoto, N. Tateiwa, F. Honda, R. Settai, Y. Ōnuki, *J. Phys.: Conf. Ser.* 273 (2011) 012122.
- [16] R. Troć, M. Pasturel, O. Tougait, M. Potel, H. Noël, *Intermetallics* 19 (2011) 913-918.
- [17] R. Troć, M. Samsel-Czekąła, E. Talik, R. Wawryk, Z. Gajek, M. Pasturel, *Phys. Rev. B* 92 (2015) 104427.
- [18] M. Samsel-Czekąła, E. Talik, M. Pasturel, R. Troć, *J. Alloys Compd.* 554 (2013) 438-445.
- [19] A.I. Tursina, N.G. Bukhan'ko, A.V. Gribanov, H. Noël, T. Roisnel, Y.D. Seropegin, *J. Alloys Compd.* 400 (2005) 194-196.
- [20] *SADABS: Area-Detector Absorption Correction*; Siemens Industrial Automation, Inc., Madison, WI, 1996.
- [21] A. Altomare, M.C. Burla, M. Camalli, G.L. Casciarano, C. Giacovazzo, A. Guagliardi, A.G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [22] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112.
- [23] L.M. Gelato, E. Parthé, *J. Appl. Crystallogr.* 20 (1987) 139.
- [24] K. Brandenburg, *Diamond*, Version 2.1b, Crystal Impact GbR, 1999.
- [25] O. Tougait, J. Stepien Damm, V.I. Zaremba, H. Noël, R. Troć, *J. Solid State Chem.* 174 (2003) 152-158.
- [26] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data : Crystal Structure Database for Inorganic Compounds*, Release 2009/1, ASM International, Materials Park, Ohio, USA, and references therein.
- [27] E. Teatum, K. Gschneidner, J. Waber, In: *Compilation of Calculated Data Useful in Predicting Metallurgical Behavior of the Elements in Binary Alloy Systems*, LA-2345, Los Alamos Scientific Laboratory, 1960.
- [28] M. Pasturel, O. Tougait, M. Potel, T. Roisnel, K. Wochowski, H. Noël, R. Troć, *J. Phys.: Cond. Matter* 21(2009) 125401.