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Uranium cobalt tetraaluminide, $UCoAl_4$

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The structure of $UCoAl_4$ can be viewed as a succession of atomic layers, with the compositions UCoAl and Al_3, that alternate along the *c* axis. The packing within the pure Al layer at $z = \frac{1}{2}$ results from edge-sharing of triangles, squares and pentagons of Al atoms. Two successive Al_3 layers thus define pentagonal, square-based and trigonal prisms which are centred at $z = 0$ by the U, Co and remaining Al atoms. $UCoAl_4$ is a high-temperature phase that is only observed in as-cast samples.

Comment

Investigations of rare earth or actinide (*R*) intermetallic compounds which combine a transition metal (*T*) with an element of the *p* block (*X*) have led to the synthesis and characterization of numerous compounds with a wide variety of anomalous physical properties. For a given formula, compounds form between most *f*-block elements and various transition metals, as well as some *p*-block elements of the same column. In the ternary *R*–Co–Al systems, where *R* is a 4*f* or 5*f* element, the compounds $RCoAl_4$ are reported to exist with *R* = La, Ce and Pr (Rykhal' *et al.*, 1977). They adopt the orthorhombic $LaCoAl_4$ structure type (*Pmma*, *oP*12; Rykhal' *et al.*, 1977). During the study of the ternary U–Co–Al phase diagram, the novel compound $UCoAl_4$ was found in as-cast samples and its crystal structure has been determined by single-crystal X-ray diffraction.

$UCoAl_4$ adopts a new type of structure which can be described as a succession of two layers that alternate along the hexagonal *c* axis. Their compositions of UCoAl and Al_3 correspond to the basal planes lying at $z = 0$ and $z = \frac{1}{2}$, respectively. The pure Al layer ($z = \frac{1}{2}$) is formed by triangles, squares and pentagons of Al atoms assembled by edge-sharing (Fig. 1*a*). According to the Schläfli notation (Frank & Kasper, 1959), the tesselation of this slab can be described as 3454 and 3545 nets of the Al1 and Al2 sites, respectively. A double layer thus defines pentagonal, square-based and trigonal prisms, within which the U, Co and Al3 atoms are located at $z = 0$. Neighbouring atoms within the slab additionally cap all the rectangular faces of the various prisms.

The interatomic distances in $UCoAl_4$ compare well those reported for other ternary U–Co–Al compounds, such as U_2Co_2Al (Sampaio *et al.*, 1968) and $U_2Co_6Al_{19}$ (Tougait *et al.*, 2003). The structure of hexagonal $UCoAl_4$ is closely related to that of orthorhombic $LaCoAl_4$ (Fig. 1*b*). The latter structure can also be viewed as a stacking of two kinds of layers, having the compositions LaCoAl and Al_3, alternating along the short *b* axis. The main difference between the $UCoAl_4$ and $LaCoAl_4$ structures arises from a different arrangement of the building motifs within the pure Al slab, which defines a 345^2 net in the rare-earth compound.

$UCoAl_4$ is a high-temperature phase. Complete chemical and structural analyses of as-cast and heat-treated samples have confirmed the presence of this compound in the as-cast samples only. Electron microprobe analysis and powder X-ray diffraction have shown the occurrence of three phases in the as-cast samples, *viz*. hexagonal $UCoAl_4$ ($P\bar{6}2m$, *hP*18) as the major component, cubic $UAl_{2-x}Co_x$ (ternary extension of UAl_2, $MgCu_2$-type, $Fd\bar{3}m$, *cF*24; Petzow *et al.*, 1964) and monoclinic $U_2Co_6Al_{19}$ (*C*2/*m*, *mC*108; Tougait *et al.*, 2003). Annealing the samples at temperatures up to 1873 K yields a

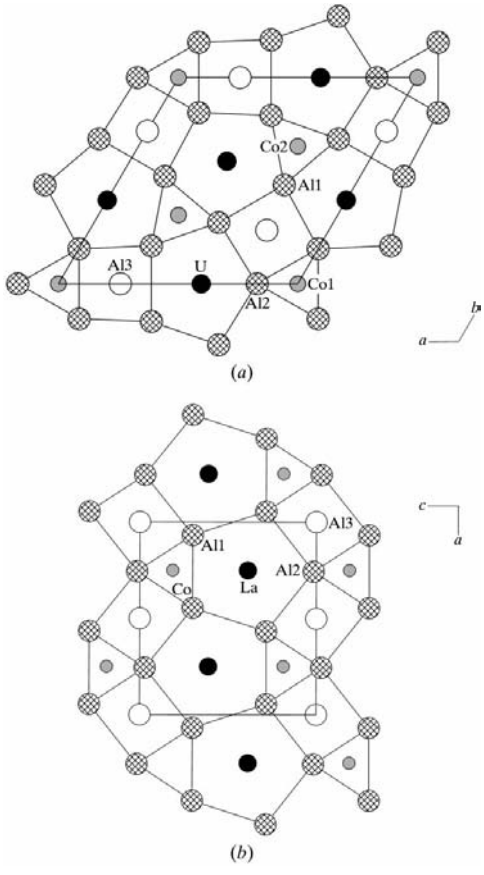

Figure 1
(*a*) $UCoAl_4$ viewed down the *c* axis. (*b*) $LaCoAl_4$ viewed down the *b* axis. Open and filled circles represent atoms at $z = 0$ and hatched circles represent atoms at $z = \frac{1}{2}$.

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three-phase mixture of cubic $UAl_{2-x}Co_x$, cubic $UAl_{3-x}Co_x$ (ternary extension of UAl_3, $AuCu_3$, $Pm\bar{3}m$, $cP4$; Lupşa *et al.*, 1994) and orthorhombic $U_2Co_3Al_9$ ($Y_2Co_3Ga_9$-type, *Cmcm*, *oC*56; Grin' *et al.*, 1984). Thus, $UCoAl_4$ decomposes according to the peritectic reaction $UCoAl_4 \rightarrow UAl_{3-x}Co_x + U_2Co_3Al_9$. Due to the absence of single-phase samples, the complete investigation and interpretation of the magnetic properties of $UCoAl_4$ has not yet been carried out.

Experimental

Samples with U:Co:Al atomic ratios of 1:1:4 were prepared by standard arc-melting techniques. Ingots were placed in alumina crucibles and sealed in fused silica tubes under a residual atmosphere of argon for heat-treatment at 1173 K for 500 h, or annealed at 1873 K for 10 h using a high-frequency furnace. Single crystals of $UCoAl_4$ could be extracted from crushed as-cast samples. X-ray diffraction powder patterns were collected using monochromatic Cu $K\alpha_1$ radiation and Co $K\alpha$ radiation. Scanning electron microscopy and energy dispersive spectroscopy (SEM–EDS) were performed on samples embedded in resin and polished using SiC paper and diamond paste down to 1 µm. A thin layer of gold was deposited on their surfaces before metallographic analyses.

Crystal data

$UCoAl_4$
M_r = 404.88
Hexagonal, $P\bar{6}2m$
a = 9.1610 (10) Å
c = 4.1140 (10) Å
V = 299.01 (9) Å^3
Z = 3
D_x = 6.746 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2952 reflections
θ = 4.5–46.0°
μ = 45.38 mm^{-1}
T = 293 (2) K
Prism, black
0.11 × 0.02 × 0.02 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
Absorption correction: analytical (*SHELXL*70 in *CrysAlis*; Oxford Diffraction, 2003)
T_{min} = 0.038, T_{max} = 0.468
5480 measured reflections
1001 independent reflections
949 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 46.1°
$h = -18 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -8 \rightarrow 5$

Refinement

Refinement on F^2
$R(F)$ = 0.022
$wR(F^2)$ = 0.037
S = 1.01
1001 reflections
25 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.42 e Å^{-3}
$\Delta\rho_{min}$ = −1.91 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0154 (5)
Absolute structure: Flack (1983), 561 Friedel pairs
Flack parameter = 0.046 (7)

Table 1
Selected interatomic distances (Å).

U—Co2^{i}	2.7834 (3)	Al2—Al3^{vi}	2.9259 (13)
U—Al3	3.085 (2)	Al2—U^{vii}	2.9806 (13)
U—Al1^{ii}	3.1516 (10)	Al3—Co1^{viii}	2.364 (2)
U—Al1^{iii}	3.1967 (10)	Al3—Al1^{ix}	2.7851 (14)
Co2—U^{iv}	2.7834 (3)	Al3—Al2^{x}	2.9259 (13)
Al1—U^{v}	3.1516 (10)	Al3—U^{x}	3.2547 (5)
Al1—U^{iv}	3.1967 (10)		

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, -x+y, 1-z$; (iii) $-x+y, -x, z-1$; (iv) $-y, x-y, z$; (v) $1-x+y, 1-x, z$; (vi) $-y, x-y-1, 1+z$; (vii) $x, y, 1+z$; (viii) $1+x, y, z$; (ix) $1-y, x-y, z-1$; (x) $1-y, x-y, z$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1029). Services for accessing these data are described at the back of the journal.

References

Bergerhoff, G. (1996). *DIAMOND*. Version 2.0. Gerhard-Domagk-Straße 1, 53121 Bonn, Germany.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Frank, F. C. & Kasper, J. S. (1969). *Acta Cryst.* **12**, 483–499.
Grin', Yu. N., Gladyshevskii, R. E., Sichevich, O. M., Zavodnik, V. E., Yarmolyuk, Ya. P. & Rozhdestvenskaya, I. V. (1984). *Sov. Phys. Crystallogr.* **29**, 528–530.
Lupşa, I., Lucaci, P. & Burzo, E. (1994). *J. Alloys Compd*, **204**, 247–250.
Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.70. Oxford Diffraction Ltd, Abingdon, England.
Petzow, G., Steeb, S. & Kiessler, G. (1964). *J. Nucl. Mater.* **12**, 271–276.
Rykhal', R. M., Zarechnjuk, O. S. & Jarmoljuk, Ja. P. (1977). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, **39**, 265–268. (In Russian.)
Sampaio, A. O., Santa Marta, E., Lukas, H. L. & Petzow, G. (1968). *J. Less Common Met.* **14**, 472–473.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Tougait, O., Stêpieň-Damm, J., Zaremba, V., Noël, H. & Troč, R. (2003). *J. Solid State Chem.* **174**, 152–158.