

Uranium and aluminium order–disorder
in $U_{1-x}Pt_2Al_{7-6x}$ [$x = 0.33$ (1)]Svilen Bobev,^{a*} Eric D. Bauer^b
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The new ternary title compound, uranium diplatinum penta-aluminium, has been synthesized from a reaction of the corresponding elements at 1273 K. It crystallizes in the rare hexagonal $Ce_2Pt_6Ga_{15}$ structure type, where one-third of the U atoms are randomly replaced by triangles of Al atoms. Possible ordered models in hexagonal and *ortho*-hexagonal supercells were tried without success. All the atoms occupy special positions: U ($\bar{6}m2$), Pt ($3m.$), and Al ($mm2$, $3m.$ and $3m.$).

Comment

The hybridization of the uranium *5f* electrons with the *s*, *p*, and *d* states of the neighboring atoms in U-containing intermetallic phases is believed to be the main factor governing the properties of such compounds. Over the past two or three decades, a great number of uranium-based materials have been synthesized and their properties determined (Freeman & Lander, 1984). Notably, unconventional superconductivity,

Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean σ (Pt–Al) = 0.002 Å
Disorder in main residue
 R factor = 0.020
 wR factor = 0.039
Data-to-parameter ratio = 8.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

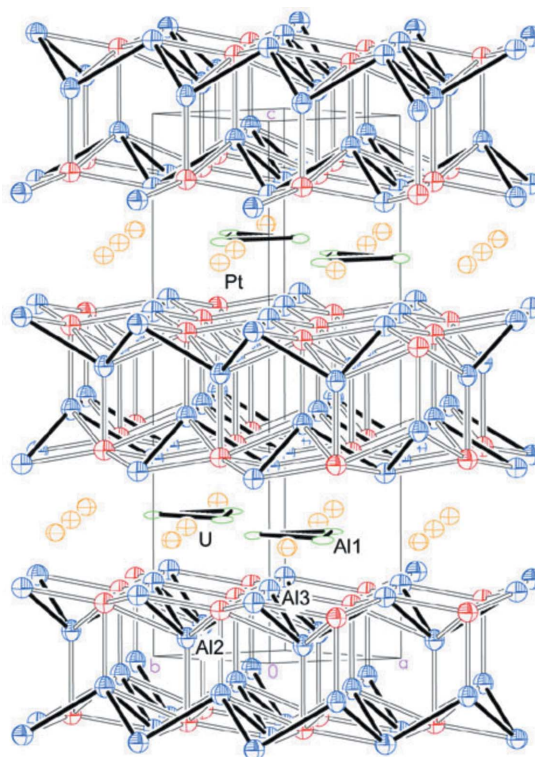


Figure 1

A view of (I) projected approximately along [110]. Displacement ellipsoids are drawn at the 95% probability level. The U atoms are drawn as yellow ellipsoids with principal ellipses, the Pt atoms as red ellipsoids with octant shading, and atoms Al2 and Al3 as blue ellipsoids with octant shading. The disordered Al1 atoms are represented with outline green ellipsoids. The unit cell is outlined.

heavy fermion and/or Kondo behavior have been reported for many compounds, such as UBe_{13} (Ott *et al.*, 1983), $\text{U}_3\text{Ni}_5\text{Al}_{19}$ (Bauer *et al.*, 2005), UPt_3 (Frings *et al.*, 1983), U_2Zn_{17} (Ott *et al.*, 1984), the families of UTSb_2 (Kaczorowski *et al.*, 1998; Bobev *et al.*, 2006*a,b*) and UTGa_5 compounds (Moreno *et al.*, 2005), where T = transition metal.

Our interest in the low-temperature properties of various $5f$ -intermetallics coupled with systematic exploratory syntheses employing flux-growth techniques (Canfield & Fisk, 1992) led us to the discovery of a new family of ternary intermetallics, $\text{UT}_2\text{Zn}_{20}$ (T = late $4d$ transition metal), isostructural with $\text{UFe}_2\text{Zn}_{20}$ (Goncalves *et al.*, 1998). Attempts to extend these studies to the $5d$ transition metals, in particular Ir and Pt, failed: under the zinc flux reaction conditions, a reduction of the alumina crucible takes place (see *Experimental*) and the crystals that result are the γ -brass type $\text{Ir}_3\text{Zn}_{10}$ (Villars & Calvert, 1991) and the aluminium-rich title compound, (I).

Compound (I) crystallizes with the rare hexagonal $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ structure type (Kwei *et al.*, 1996), and its structure can be viewed as being built up from corrugated double layers of PtAl_2 , which are separated by hexagonal nets of U atoms (Fig. 1). An interesting feature of the structure of (I) is that one-third of the U atoms are randomly substituted by Al_3 triangles. A very similar statistical disorder of Ce and Ga atoms has been suggested to be the reason for the highly anisotropic properties of the parent compound, $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ [note that the formulations $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ and $\text{Ce}_4\text{Pt}_{12}\text{Ga}_{30}$ (Villars & Calvert, 1991) are used for convenience only; the actual unit cell contains Ce at Wyckoff position $2c$ (67% occupied), Pt at $4f$, and Ga1 at $6h$ (33% occupied), Ga2 at $4f$ and Ga3 at $4e$].

The disorder in the structure of $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ has been studied by means of single-crystal X-ray and neutron diffraction, as well as powder neutron diffraction and EXAFS (Kwei *et al.*, 1996), and demonstrated to be fully statistical; evidence of weak diffuse scattering is clearly observed in the neutron diffraction data, suggesting that disorder arises from a lack of registration of successive Ce_2Ga_3 layers. Using this disorder model, the U–Al disorder in (I) can be understood in a similar way: whenever the U atoms are missing in the hexagonal layer (randomly, *ca* one-third of the time), the vacancy is filled with an Al_3 triangle (Fig. 2).

The fact that the refinement of the site occupancies of U and Al1 yield values of almost exactly 67 and 35%, respectively, suggests that a hexagonal (with $V_s = 3V_c$; V = cell volume, s = supercell, c = cell used here) or *ortho*-hexagonal [with $V_s = 3(3^{\frac{1}{2}}V_c)$] lattice might allow for a refinement with ordered fully occupied U and Al positions (Fig. 2). However, just as with $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$, lowering the symmetry to the trigonal subgroup $P\bar{3}1c$ (with the same cell parameters), or tripling the cell volume and refining the structure in various trigonal or hexagonal space groups, did not provide any evidence for ordering. Attempts to find an ordered superstructure with $3(3^{\frac{1}{2}})$ times the volume of the hexagonal subcell also failed, from which we conclude that long-range ordering of U and Al1 in (I) does not exist.

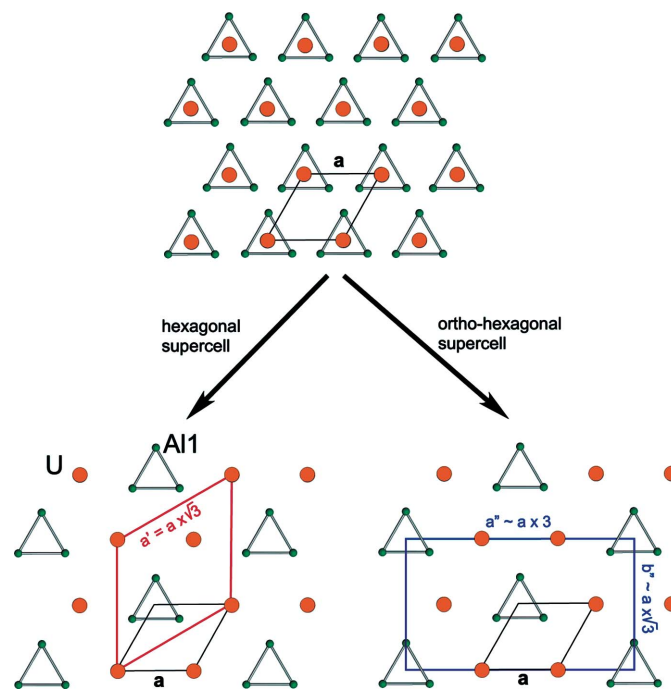


Figure 2

A schematic representation of the disordered U_2Al_3 layer in (I) (top view), where every third U is missing, leaving a vacancy filled by Al_3 triangles. Possible ordering of these defects in hexagonal (lower left) and *ortho*-hexagonal (lower right) supercells is also drawn. Relevant interatomic distances are given in Table 1.

Compound (I) is only the second ternary compound in the U–Pt–Al phase diagram to be structurally characterized. The other example, the equiatomic UPtAl (also hexagonal, ZnNiAl-type, an ordered variant of the common Fe_2P -type) is a ferromagnet below 43 K with strong uniaxial anisotropy (Andreev *et al.*, 2001). Preliminary measurements on the title compound also suggest interesting low-temperature properties, and attempts to grow crystals of (I) from an Al flux are currently underway.

Experimental

A mixture of the metals, in a stoichiometric ratio U:Pt:Zn = 1:2:30 (intended to produce cubic $\text{UPt}_2\text{Zn}_{20}$ but loaded with an excess of Zn to serve as a flux), was placed in a 5 ml alumina crucible, which was subsequently enclosed in a fused-silica ampoule and flame-sealed under vacuum. The ampoule was heated at 1273 K for 2 h and then cooled at a rate of 30 K h^{-1} to 873 K, when it was removed from the furnace. The excess of molten Zn was removed by centrifugation.

Crystal data

$\text{U}_{0.67}\text{Pt}_2\text{Al}_5$
 $M_r = 684.56$
 Hexagonal, $P6_3/mmc$
 $a = 4.2929(8) \text{ \AA}$
 $c = 16.276(6) \text{ \AA}$
 $V = 259.77(12) \text{ \AA}^3$
 $Z = 2$
 $D_x = 8.752 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 2248 reflections
 $\theta = 2.5\text{--}28.1^\circ$
 $\mu = 75.26 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Irregular fragment, grey
 $0.06 \times 0.04 \times 0.03 \text{ mm}$

Data collection

Bruker SMART APEX diffractometer	154 independent reflections
ω scans	135 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.057$
$T_{\text{min}} = 0.047$, $T_{\text{max}} = 0.105$	$\theta_{\text{max}} = 28.1^\circ$
2248 measured reflections	$h = -5 \rightarrow 5$
	$k = -5 \rightarrow 5$
	$l = -19 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.039$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 1.00 \text{ e } \text{\AA}^{-3}$
154 reflections	$\Delta\rho_{\text{min}} = -1.50 \text{ e } \text{\AA}^{-3}$
19 parameters	Extinction correction: SHELXL97
	Extinction coefficient: 0.0038 (4)

Table 1

Selected bond lengths (\AA).

U—Al1	3.087 (7)	Pt—Al2 ^{iv}	2.685 (2)
U—Al3	3.101 (3)	Pt—U ^v	3.3765 (8)
Pt—Al1 ⁱ	2.493 (4)	Al1—Al1 ^{vi}	2.598 (18)
Pt—Al3 ⁱⁱ	2.5154 (9)	Al1—Al3	2.855 (3)
Pt—Al2 ⁱⁱⁱ	2.521 (5)	Al2—Al2 ^{vii}	2.891 (5)

Symmetry codes: (i) $x - y, x, -z + 1$; (ii) $-x, -y + 1, z + \frac{1}{2}$; (iii) $x, y, -z + \frac{1}{2}$; (iv) $-x + 1, -y + 1, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $-y, x - y - 1, z$; (vii) $-x + 1, -y + 1, -z$.

Initial refinements assuming a fully stoichiometric formula of UPt_2Al_7 led to unrealistic displacement factors for Al1 and U. Also, the U—Al1 distance was unreasonably short, *ca* 1.5 \AA , suggesting partial occupancy for the U and Al1 sites. Similar disorder is known for the archetype $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ (Kwei *et al.*, 1996). This was verified by freeing the site occupation factor for an individual atom, while other remaining parameters were kept fixed. The refined occupancy for the U site is 0.670 (4), whereas Al1 refined as 0.349 (14) occupied. The refined occupancy factors for the other sites did not deviate significantly from fully occupied (98 to 102%) and were reset to full occupancy for the final cycles of refinement. The maximum difference peak and deepest difference hole are located 1.22 \AA from Pt, and 1.86 \AA from Al3, respectively. Note: The coordinates reported here are those obtained after standardization using the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). This interchanges the

labels of the 6*h* and 4*e* sites; Al1 and Al3 here *versus* Ga3 and Ga1 in $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$ (Kwei *et al.*, 1996), respectively.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

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