

Svilen Bobev,^{a*} Daniel J. Mixson,^b Eric D. Bauer^b and John L. Sarrao^b^aDepartment of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA, and ^bMaterials Science and Technology Division, Los Alamos National Laboratory, MS K764, Los Alamos, NM 87545, USA

Correspondence e-mail: sbobev@chem.udel.edu

Key indicatorsSingle-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\lambda) = 0.000$ Å
Disorder in main residue
 R factor = 0.020
 wR factor = 0.047
Data-to-parameter ratio = 11.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Partial Pd occupancy in uranium palladium diantimonide, $\text{UPd}_{0.603(6)}\text{Sb}_2$**

Single crystals of uranium palladium diantimonide, $\text{UPd}_{0.603(6)}\text{Sb}_2$, were grown from an Sb flux. The title compound crystallizes in space group $P4/nmm$, adopting the ZrCuSi_2 structure type, but with a partial occupancy of the Pd site. All atoms are located on special positions with site symmetries $\bar{4}m2$ for Pd and one Sb atom, and $4mm$ for U and the other Sb atom.

Received 13 February 2006
Accepted 15 February 2006**Comment**

Over the past three decades, increased attention has been paid to many intermetallic phases containing uranium and transition elements, sparked by the unique properties that these materials exhibit, such as superconductivity, heavy fermion and/or Kondo behavior and valence fluctuations (Freeman & Lander, 1984). Among these, the family of UTAs_2 and UTSb_2 compounds (where $T = 3d, 4d$ and $5d$ transition metals) have been of particular interest (Kaczorowski *et al.*, 1998; Bukowski, Gofryk *et al.*, 2005; Tran *et al.*, 2005; Bukowski *et al.*, 2004; Plackowski *et al.*, 2005). These phases crystallize with the tetragonal ZrCuSi_2 -type structure (Villars & Calvert, 1991), and their structures can be viewed as consisting of infinite PbO -type transition metal–pnictide layers, which are separated by square nets of As or Sb atoms, and U atoms occupying the space between them (Fig. 1).

According to the original report on the structure and properties of the UTSb_2 compounds ($T = \text{Fe, Co, Ni, Cu, Ru}$,

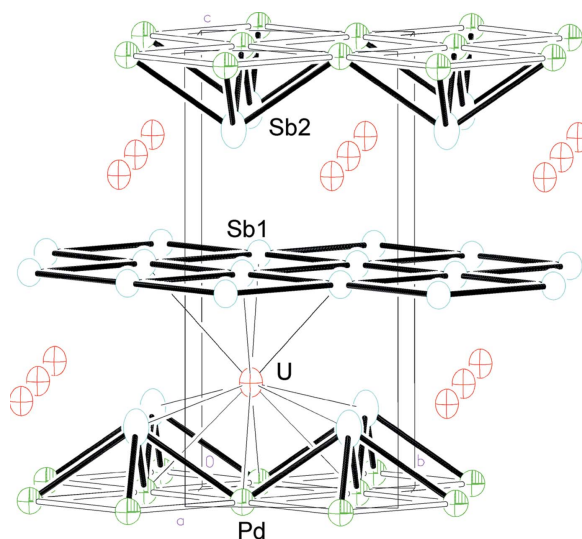


Figure 1
A view of $\text{UPd}_{0.603(6)}\text{Sb}_2$ projected approximately along $[100]$. Displacement ellipsoids are drawn at the 95% probability level. U atoms are drawn as red ellipsoids with principal ellipses, Pd atoms as green ellipsoids with octant shading, and Sb atoms as ellipsoid outlines only. The unit cell is outlined.

Pd, Ag and Au), these materials are line compounds (Kaczorowski *et al.*, 1998). However, quite recently several papers were published where the crystal structures and properties of $\text{UCu}_{0.9}\text{Sb}_2$ (Bukowski, Troc *et al.*, 2005), $\text{UCo}_{0.5}\text{Sb}_2$ (Bukowski *et al.*, 2004) and $\text{UNi}_{0.5}\text{Sb}_2$ (Plackowski *et al.*, 2005; Bukowski, Gofryk *et al.*, 2005) have been reexamined. More recently, our own synthetic efforts led to the formation of $\text{UCu}_{0.44(1)}\text{Sb}_2$ (Bobev *et al.*, 2006), a Cu-poorer variant of $\text{UCu}_{0.9}\text{Sb}_2$. All of the above suggest a potential large stoichiometry breadth for the members of the whole UT_xSb_2 family.

This conclusion is firmly supported by the structure refinement of the title compound with partial Pd occupancy. This fact, together with the apparent differences in the corresponding unit-cell parameters, specifically the c axis, 9.330 Å for $\text{UPd}_{0.60}\text{Sb}_2$ (this work) and 9.552 Å for fully occupied UPdSb_2 (Kaczorowski *et al.*, 1998), provides further evidence that the transition metal content in this and other isostructural UT_xSb_2 compounds can vary substantially. Such large homogeneity ranges are also known for many rare-earth analogs (Mills *et al.*, 2002; Tobash & Bobev, 2005), and may account for some problems with the reproducible measurements of the electronic and magnetic properties of these materials. Evidently, samples prepared by different techniques will most likely have different amounts of transition metals in the structure. This, in turn, can subtly affect the hybridization of the U $5f$ electrons with the s , p and d states of the neighboring atoms, which is believed to be the main factor governing the properties of these compounds.

Experimental

All metals used were with stated purity 99.9% or higher (U – Los Alamos, Pd and Sb – Alfa). A mixture of the reactants, in the stoichiometric ratio U:Pd:Sb = 1:1:9 (with an excess of Sb to serve as a flux), was placed in a 5 cm³ alumina crucible within an evacuated fused-silica ampoule. The ampoule was heated at 1423 K for 2 h, and cooled at 30 K h⁻¹ to 1073 K, when it was removed from the furnace. The excess of molten Sb was removed by centrifugation. Small plate-like crystals of $\text{UPd}_{0.603(6)}\text{Sb}_2$ were obtained as a single-phase product of the reaction according to the corresponding X-ray powder patterns.

Crystal data

$\text{UPd}_{0.60}\text{Sb}_2$	Mo $K\alpha$ radiation
$M_r = 545.37$	Cell parameters from 1893 reflections
Tetragonal, $P4/nmm$	$\theta = 2.2\text{--}27.3^\circ$
$a = 4.3459(7)$ Å	$\mu = 63.74$ mm ⁻¹
$c = 9.330(3)$ Å	$T = 120(2)$ K
$V = 176.21(7)$ Å ³	Bar (cut from plate), gray
$Z = 2$	$0.08 \times 0.05 \times 0.05$ mm
$D_x = 10.279$ Mg m ⁻³	

Data collection

Bruker SMART APEX CCD diffractometer	150 independent reflections
ω scans	149 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.043$, $T_{\text{max}} = 0.057$	$\theta_{\text{max}} = 27.3^\circ$
1893 measured reflections	$h = -5 \rightarrow 5$
	$k = -5 \rightarrow 5$
	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 0.8733P]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.047$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.16$	$\Delta\rho_{\text{max}} = 1.58$ e Å ⁻³
150 reflections	$\Delta\rho_{\text{min}} = -1.79$ e Å ⁻³
13 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.0067 (8)

Table 1

Selected bond lengths (Å).

U–Pd	3.1224 (7)	Sb1–Sb1 ⁱⁱ	3.0730 (5)
U–Sb2 ⁱ	3.1591 (6)	Pd–Pd ⁱⁱⁱ	3.0730 (5)
U–Sb1	3.2543 (7)		

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 2, -y + 1, -z$.

For the present refinement origin choice 2 of space group $P4/nmm$ was selected. Initial refinements assuming a fully stoichiometric formula led to displacement parameters for Pd that were *ca* 50% greater than those of the U and Sb atoms. Moreover, these refinements converged with poor residuals. Introducing a partial occupancy for the Pd site led to more realistic displacement parameters and to significantly better R factors. The occupancies for all sites were verified by freeing the site occupation factor for an individual atom, while other remaining parameters were kept fixed. The refined occupancy for the Pd site was 0.603 (6). The maximum peak and deepest hole are located 0.83 Å away from U and 2.17 Å away from Sb1, respectively.

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

This work was funded by a University of Delaware start-up grant.

References

- Bobev, S., Mixson, D. J., Bauer, E. D. & Sarrao, J. L. (2006). *Acta Cryst.* **E62**, i66–i68.
- Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bukowski, Z., Gofryk, K., Plackowski, T. & Kaczorowski, D. (2005). *J. Alloys Compd.* **400**, 33–36.
- Bukowski, Z., Tran, V. H., Stepien-Damm, J. & Troc, R. (2004). *J. Solid State Chem.* **177**, 3934–3938.
- Bukowski, Z., Troc, R., Stepien-Damm, J., Sulkowski, C. & Tran, V. H. (2005). *J. Alloys Compd.* **403**, 65–70.
- Freeman, A. J. & Lander, G. H. (1984). *Handbook on the Physics and Chemistry of the Actinides*, Vol. 1. Amsterdam: North Holland.
- Kaczorowski, D., Kruk, R., Sanchez, J. P., Malaman, B. & Wastin, F. (1998). *Phys. Rev. B*, **58**, 9227–9237.
- Mills, A. M., Lam, R., Ferguson, M. J., Deakin, L. & Mar, A. (2002). *Coord. Chem. Rev.* **233**, 207–222.
- Plackowski, T., Kaczorowski, D. & Bukowski, Z. (2005). *Phys. Rev. B*, **72**, 184418.
- Sheldrick, G. M. (2001). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
- Tobash, P. H. & Bobev, S. (2005). *Acta Cryst.* **E61**, i191–i192.
- Tran, V. H., Troc, R., Bukowski, Z., Budurski, D. & Sulkowski, C. (2005). *Phys. Rev. B*, **71**, 094428.
- Villars, P. & Calvert, L. D. (1991). *Pearson's Handbook of Crystallographic Data for Intermetallic Compounds*, 2nd ed. Materials Park, Ohio, USA: American Society for Metals.