# inorganic papers

Svilen Bobev,[a]* Daniel J. Mixson,[b] Eric D. Bauer[b] and John L. Sarrao[b]

[a]Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA, and [b]Materials Science and Technology Division, Los Alamos National Laboratory, MS K764, Los Alamos, NM 87545, USA

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

Uranium copper diantimonide, $UCu_{0.44(1)}Sb_2$ with a large Cu deficiency

$UCu_{0.44(1)}Sb_2$, synthesized in the presence of an Sb flux, crystallizes in the $ZrCuSi_2$-type structure, but with a partial occupancy of the Cu site.

Comment

Ternary intermetallics containing uranium and transuranic metals have attracted increased interest over the past few decades owing to the occurrence of phenomena such as superconductivity, heavy fermion and/or Kondo behavior, and valence fluctuations (Freeman & Lander, 1984). Very recently, particular attention has been paid to $UTSb_2$ compounds where T = 3d, 4d and 5d transition metals (Kaczorowski et al., 1998; Bukowski et al., 2004; Bukowski, Gofryk et al., 2005; Tran et al., 2005; Plackowski et al., 2005, Bobev et al., 2006). These phases crystallize with the tetragonal $ZrCuSi_2$-type structure (Villars & Calvert, 1991), which can be viewed as consisting of infinite corrugated PbO-type CuSb layers, which are separated by
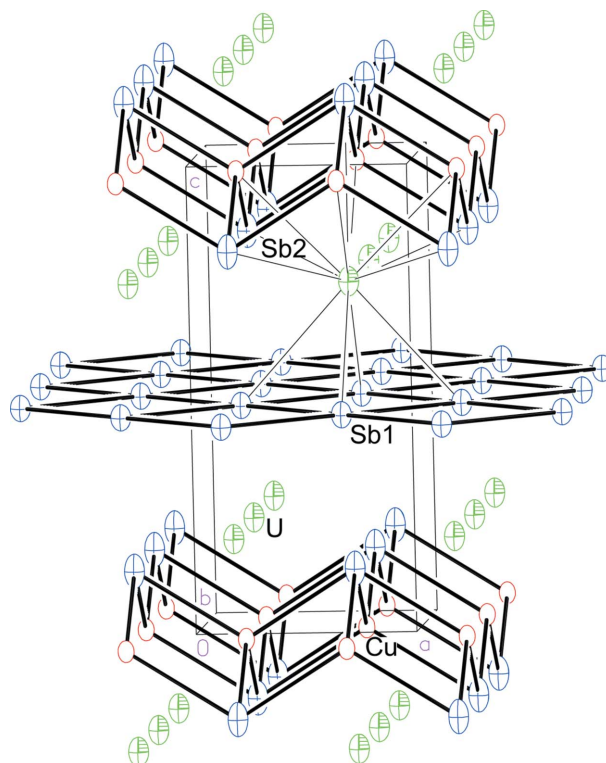
Figure 1
A view of $UCu_{0.44}Sb_2$ projected approximately along [010]. Displacement ellipsoids are drawn at the 95% probability level. U atoms are drawn as green ellipsoids with octant shading, Cu atoms as ellipsoid outlines only, and Sb atoms as blue ellipsoids with principal ellipses. The unit cell is outlined.

square nets of Sb atoms and U atoms occupying the space between them (Fig. 1).

The first report on the structure and properties of a series of $UTSb_2$ compounds (T = Fe, Co, Ni, Cu, Ru, Pd, Ag and Au) does not discuss any possible phase breadth (Kaczorowski *et al.*, 1998); however, the same team has recently published several papers where the crystal structures and properties of $UCo_{0.5}Sb_2$ and $UNi_{0.5}Sb_2$ have been reexamined (Bukowski *et al.*, 2004; Plackowski *et al.*, 2005). Another recent publication reports refined atomic positions and occupation factors for $UCu_{0.9}Sb_2$ (Bukowski, Troc *et al.*, 2005), and suggests that previously overlooked large stoichiometry breadth might be an inherent feature for the whole UT_xSb_2 family.

Our refinement of the structure of UCu_xSb_2 from single-crystal X-ray data confirms the latter observation and provides further evidence that the transition metal content can vary substantially – the refined occupancy for the Cu site is 0.44 (1) compared with 0.9 obtained for crystals produced *via* different synthetic route (Bukowski, Troc *et al.*, 2005). These differences in the crystal structure are also clearly seen in the corresponding differences in the unit-cell parameters, specifically the c axis: 9.176 Å for $UCu_{0.44}Sb_2$ (this work), 9.543 Å for $UCu_{0.9}Sb_2$ (Bukowski, Troc *et al.*, 2005) and 9.643 Å for $UCuSb_2$ (Kaczorowski *et al.*, 1998). There are many precedents for such large non-stoichiometry in related $CeCu_xSb_2$ compounds (Muro *et al.*, 1997; Tobash & Bobev, 2005).

Inspection of the cell parameters of the whole $UTSb_2$ series clearly shows large variations (from *ca* 9.08 Å for $UNiSb_2$ to *ca* 10.28 Å for $UAgSb_2$; Kaczorowski *et al.*, 1998). Evidently, the homogeneity range is rather large and may account for some problematic interpretations of the electronic and magnetic properties of these materials. Samples prepared by different techniques will most likely yield UT_xSb_2 with different values of x. Such differences will have far-reaching implications on the analyses of the corresponding physical properties as the electron count will vary greatly with x. 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

A mixture of reactants, in the stoichiometry U:Cu:Sb = 1:1:20 with a nearly tenfold excess of Sb 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 4 h and cooled at 2 K h⁻¹ to 923 K, when it was removed from the furnace. The excess of molten Sb was removed by centrifugation.

Crystal data

$UCu_{0.44}Sb_2$	Mo $K\alpha$ radiation
$M_r = 509.49$	Cell parameters from 1295
Tetragonal, $P4/nmm$	reflections
$a = 4.3289$ (8) Å	$\theta = 2.2$–$26.3°$
$c = 9.176$ (3) Å	$\mu = 64.92$ mm⁻¹
$V = 171.95$ (7) Å³	$T = 120$ (2) K
$Z = 2$	Block, gray
$D_x = 9.840$ Mg m⁻³	$0.06 \times 0.05 \times 0.05$ mm

Data collection

Bruker SMART APEX	134 independent reflections
diffractometer	134 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan	$\theta_{max} = 26.3°$
($SADABS$; Sheldrick, 2003)	$h = -5 \rightarrow 5$
$T_{min} = 0.040$, $T_{max} = 0.053$	$k = -5 \rightarrow 5$
1295 measured reflections	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$+ 1.0837P]$
$wR(F^2) = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.42$	$(\Delta/\sigma)_{max} < 0.001$
134 reflections	$\Delta\rho_{max} = 1.27$ e Å⁻³
13 parameters	$\Delta\rho_{min} = -1.90$ e Å⁻³
	Extinction correction: $SHELXL97$
	Extinction coefficient: 0.0221 (18)

Table 1
Selected bond lengths (Å).

U—Cu	3.0711 (8)	Sb1—Sb1ⁱⁱ	3.0610 (6)
U—Sb2ⁱ	3.1678 (7)	Sb2—Cuⁱⁱⁱ	2.5579 (9)
U—Sb1	3.2387 (9)		

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

Initial refinements assuming a fully stoichiometric formula led to displacement parameters for Cu that were more that 50% greater than the displacement parameters of the U and Sb sites, suggesting a partial occupancy of the Cu site. The occupancies for all sites were verified by freeing the site occupation factor for an individual atom, while the remaining parameters were kept fixed. The refined occupancy of the Cu site was 0.44 (1). The maximum peak and deepest hole are located 0.85 Å away from U and 0.95 Å away from Sb2, 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* (Sheldrick, 2001); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

References

Bobev, S., Mixson, D. J., Bauer, E. D. & Sarrao, J. L. (2006). *Acta Cryst.* E**62**, i64–i65.
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.
Muro, Y., Takeda, N. & Ishikawa, M. (1997). *J. Alloys Compd.* **257**, 23–29.
Plackowski, T., Kaczorowski, D. & Bukowski, Z. (2005). *Phys. Rev. B*, **72**, 184418.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.

Tobash, P. H. & Bobev, S. (2005). *Acta Cryst.* E**61**, 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.