

Partial Cu occupancy in uranium copper diantimonide, $\text{UCu}_{0.60(4)}\text{Sb}_2$

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The title compound, $\text{UCu}_{0.60(4)}\text{Sb}_2$, crystallizes in the tetragonal space group $P4/nmm$. The U atom and one independent Sb atom have $4mm$ site symmetry, whereas the Cu atom and the other Sb atom have $\bar{4}2m$ site symmetry. Zigzag USb sheets stack perpendicular to the c axis. These sheets are separated by square-planar nets of Sb atoms and Cu atoms. The length of the a axis for UCu_xSb_2 is invariant to x , whereas there is a linear relationship between Cu occupancy and the length of the c axis (following Vegard's Law) that holds for x between 0 and 1. This is explained in terms of the crystal structure.

Comment

$\text{UCu}_{0.60(4)}\text{Sb}_2$ crystallizes with two formula units in the tetragonal space group $P4/nmm$. It possesses the HfCuSi_2 structure type (Andrukhiv *et al.*, 1975). Zigzag U1Sb1 sheets stack perpendicular to the c axis (Fig. 1). These sheets are separated by square-planar nets of Sb2 atoms and Cu1 atoms, the repeating pattern being (a) Sb2 planar net, (b) U1Sb1 sheet, (c) Cu1 planar net, and (d) U1Sb1 sheet [aligned antiparallel in the c direction to the (b) sheet]. The U1 and Sb1 atoms have $4mm$ site symmetry, whereas the Cu1 and Sb2 atoms have $\bar{4}2m$ site symmetry. The U1 atoms are surrounded by a square antiprism of Sb1 and Sb2 atoms. The geometry around the Sb1 atom is a square antiprism of Cu1 and U1 atoms. The Cu1 atoms are coordinated to four Sb1 atoms in a tetrahedral arrangement, and Sb2 atoms are coordinated to four U1 atoms, also in a tetrahedral arrangement.

Since the UMSb_2 compounds (M is a transition metal) were first reported [$M = \text{Ni}$ and Cu (Kaczorowski, 1992); $M = \text{Fe}$, Ru , Co , Pd , Ag and Au (Kaczorowski *et al.*, 1998)], they have received considerable attention, mainly because of their interesting magnetic properties, including Kondo behaviour (Kaczorowski *et al.*, 1998; Bukowski *et al.*, 2005). Large stoichiometric variations are frequently encountered in these UMSb_2 compounds, examples being $\text{UCo}_{0.46}\text{Sb}_2$ (Bukowski, Tran *et al.*, 2004) and $\text{UNi}_{0.5}\text{Sb}_2$ (Bukowski, Kaczorowski *et al.*, 2004). Such variations are also common among rare-earth analogues (Wollesen *et al.*, 1996). The compound $\text{UCu}_{0.60(4)}\text{Sb}_2$

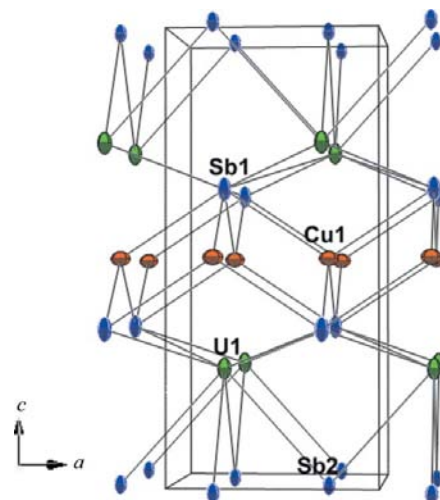


Figure 1

A view of the structure of $\text{UCu}_{0.60(4)}\text{Sb}_2$, approximately along [010]. Displacement ellipsoids are shown at the 75% probability level.

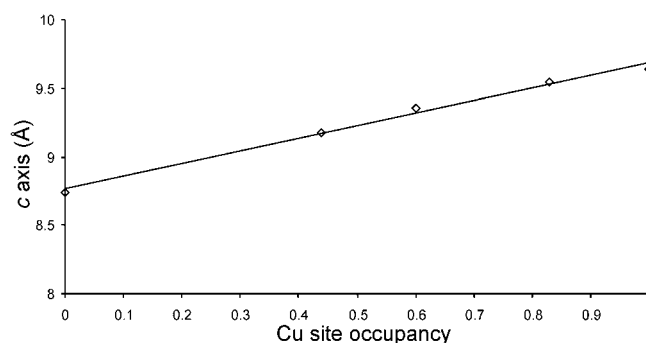


Figure 2

The dependence of the length of the c axis on x in the known UCu_xSb_2 compounds.

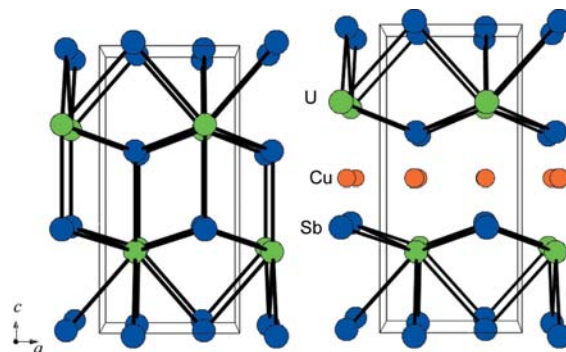


Figure 3

Comparison of the structures of USb_2 (left) and UCuSb_2 (right).

reported here is another stoichiometric variation in the UCu_xSb_2 system, for which the known compounds are $\text{UCu}_{0.44}\text{Sb}_2$ (Bobev *et al.*, 2006), $\text{UCu}_{0.83}\text{Sb}_2$ (Bukowski *et al.*, 2005) and UCuSb_2 (Kaczorowski *et al.*, 1998). Reaction conditions and starting compositions are presumably the determining factors in the final Cu occupancy. This family of compounds obeys Vegard's Law (Vegard, 1921): the cell constant c increases linearly with Cu occupancy, as shown in Fig. 2, even though the present structures were determined at

100 and 120 K and the previous structures were determined at 298 K. This linear relationship holds at all Cu occupancies, including the 'zero occupancy', *i.e.* USb_2 (Leciejewicz *et al.*, 1967). The structures of USb_2 and UCuSb_2 are indeed related (Fig. 3). In UCuSb_2 , the voids between adjacent USb zigzag sheets are filled with Cu atoms, effectively pushing the sheets apart and preventing interlayer U–Sb bonding along the *c* axis. This simple geometric consideration explains why the *c* axis lengthens but the *a* axis remains unchanged when the Cu occupancy is increased.

Experimental

USb_2 was obtained from the reaction of U powder [0.63 mmol, ORNL, prepared from turnings as described elsewhere (Klein Haneveld & Jellinek, 1969)] and Sb (1.26 mmol, Aldrich, 99.5%) in a carbon-coated fused-silica tube. The tube was heated to 1273 K in 20 h, held there for 111 h, cooled to 773 K in 20 h, and then air-cooled to 293 K. Single crystals of uranium copper antimonide, $\text{UCu}_{0.60(4)}\text{Sb}_2$, were obtained from the reaction of USb_2 (0.093 mmol) and CuO (0.093 mmol, Aldrich, 99.99%) in a carbon-coated fused-silica tube. The tube was heated to 773 K in 10 h, further heated to 973 K in 60 h, held there for 70 h, heated to 1173 K in 20 h, held there for 180 h, cooled to 773 K over a period of 100 h, and finally cooled to 293 K over a period of 60 h. The product consisted mainly of UO_2 powder and elemental Sb, among which a few small black plates were found. Energy-dispersive X-ray analysis showed the presence of U, Cu, and Sb in these plates.

Compound (I) at 100 K

Crystal data

$\text{UCu}_{0.638}\text{Sb}_2$	$Z = 2$
$M_r = 521.84$	Mo $K\alpha$ radiation
Tetragonal, $P4/nmm$	$\mu = 65.20 \text{ mm}^{-1}$
$a = 4.320 (4) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 9.341 (9) \text{ \AA}$	$0.14 \times 0.08 \times 0.05 \text{ mm}$
$V = 174.3 (3) \text{ \AA}^3$	

Data collection

Bruker SMART 1000 CCD diffractometer	1951 measured reflections
Absorption correction: numerical face-indexed (SADABS; Bruker, 2003)	155 independent reflections
$T_{\min} = 0.020$, $T_{\max} = 0.086$	155 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	13 parameters
$wR(F^2) = 0.058$	$\Delta\rho_{\text{max}} = 1.32 \text{ e \AA}^{-3}$
$S = 1.20$	$\Delta\rho_{\text{min}} = -3.32 \text{ e \AA}^{-3}$
155 reflections	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I) at 100 K.

U1–Cu ⁱ	3.132 (2)	Sb1–Cu ⁱⁱⁱ	2.593 (2)
U1–Sb ⁱ	3.167 (3)	Sb2–Sb ^{iv}	3.055 (3)
U1–Sb ⁱⁱ	3.231 (2)	Cu1–Cu ^v	3.055 (3)
Sb ⁱⁱⁱ –Cu1–Sb ⁱ	112.86 (8)		

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

Compound (I) at 120 K

Crystal data

$\text{UCu}_{0.600}\text{Sb}_2$	$Z = 2$
$M_r = 519.65$	Mo $K\alpha$ radiation
Tetragonal, $P4/nmm$	$\mu = 64.56 \text{ mm}^{-1}$
$a = 4.331 (4) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 9.355 (9) \text{ \AA}$	$0.14 \times 0.08 \times 0.05 \text{ mm}$
$V = 175.5 (3) \text{ \AA}^3$	

Data collection

Bruker SMART 1000 CCD diffractometer	1966 measured reflections
Absorption correction: numerical face-indexed (SADABS; Bruker, 2003)	160 independent reflections
$T_{\min} = 0.016$, $T_{\max} = 0.086$	157 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	13 parameters
$wR(F^2) = 0.066$	$\Delta\rho_{\text{max}} = 3.25 \text{ e \AA}^{-3}$
$S = 1.32$	$\Delta\rho_{\text{min}} = -4.14 \text{ e \AA}^{-3}$
160 reflections	

A correction was made for extinction. All atoms were given anisotropic displacement parameters. Data sets on the same crystal were collected at 100, 120, 200, and 298 K. The corresponding refined Cu occupancies were 0.634 (12), 0.600 (13), 0.608 (13), and 0.586 (12). We choose to report the value as 0.60 (4) and we report only the structure determinations at 100 and 120 K here. The structure was standardized by means of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The final difference electron densities show no significant residual peaks. The highest peaks are 1.24 and 0.07 \AA from U, and the deepest holes are 1.29 and 0.89 \AA from U at 100 and 120 K, respectively.

For both determinations, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3154). Services for accessing these data are described at the back of the journal.

References

- Andruchiv, L. S., Lysenko, L. A., Yarmolyuk, Ya. P. & Gladyshevskii, E. I. (1975). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, **7**, 645–648.
- Bobev, S., Mixson, D. J., Bauer, E. D. & Sarrao, J. L. (2006). *Acta Cryst.* **E62**, i66–i68.
- Bruker (2003). *SMART* (Version 5.054), *SAINT-Plus* (Version 6.45a) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

- Bukowski, Z., Kaczorowski, D., Stepień-Damm, J., Badurski, D. & Troc, R. (2004). *Intermetallics*, **12**, 1381–1386.
- Bukowski, Z., Tran, V. H., Stepień-Damm, J. & Troc, R. (2004). *J. Solid State Chem.* **177**, 3934–3938.
- Bukowski, Z., Troc, R., Stepień-Damm, J., Sulkowski, C. & Tran, V. H. (2005). *J. Alloys Compd.* **403**, 65–70.
- Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
- Kaczorowski, D. (1992). *J. Alloys Compd.* **186**, 333–338.
- Kaczorowski, D., Kruk, R., Sanchez, J. P., Malaman, B. & Wastin, F. (1998). *Phys. Rev. B*, **58**, 9227–9237.
- Klein Haneveld, A. J. & Jellinek, F. (1969). *J. Less Common Met.* **18**, 123–129.
- Leciejewicz, J., Troc, R., Murasik, A. & Zygmunt, A. (1967). *Phys. Status Solidi*, **22**, 517–526.
- Palmer, D. (2008). *CrystalMaker*. Version 2.0.7. CrystalMaker Software Ltd, Bicester, Oxfordshire, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Vegard, L. (1921). *Z. Phys.* **5**, 17–26.
- Wollesen, P., Jeitschko, W., Brylak, M. & Dietrich, L. (1996). *J. Alloys Compd.* **245**, L5–L8.