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## Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{Sn}-\text{Cu}) = 0.003$  Å  
Disorder in main residue  
 $R$  factor = 0.029  
 $wR$  factor = 0.079  
Data-to-parameter ratio = 10.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Copper deficiency in  $\text{UCu}_{5-x}\text{Sn}$  [ $x = 0.37(1)$ ]Received 24 March 2006  
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The ternary intermetallic title compound, known hitherto as  $\text{UCu}_5\text{Sn}$  (uranium pentacopper stannide), crystallizes with the hexagonal  $\text{CeNi}_5\text{Sn}$  structure type, and it has been presumed to be a fully stoichiometric phase, devoid of any disorder. However, the present single-crystal X-ray diffraction studies at 120 K, carried out with crystals grown from an Sn flux, suggest the existence of a previously unnoticed phase with of the title compound  $\text{UCu}_{5-x}\text{Sn}$ . All the atoms occupy special positions: U ( $\bar{6}m2$ ,  $\bar{3}m.$ ), Sn ( $3m.$ ) and Cu ( $.m.$ ,  $3m.$ , and two positions with  $\bar{6}m2$ ).

## Comment

$\text{UCu}_5\text{Sn}$  has been known since 1999 (Stepien-Damm *et al.*, 1999) to crystallize with the hexagonal  $\text{CeNi}_5\text{Sn}$  structure type (Villars & Calvert, 1991). Shortly after, neutron diffraction experiments confirmed magnetic order below 53 K with an anomalous temperature dependence of the cell parameters below  $T_C$  (Tran *et al.*, 1999).

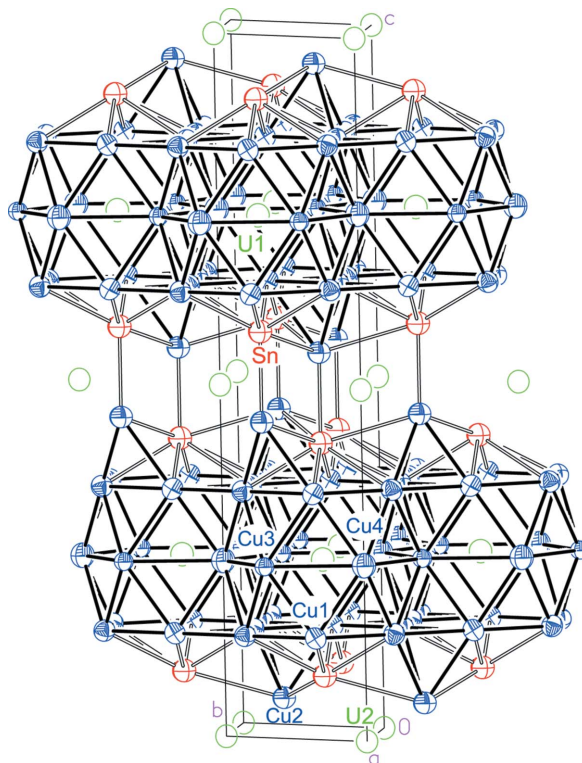


Figure 1

A view of the  $\text{UCu}_{4.63(1)}\text{Sn}$  structure, projected approximately along the direction of the  $a$  axis. Displacement ellipsoids are drawn at the 95% probability level. U atoms are drawn as green outline ellipsoids, Sn atoms as red octant shaded ellipsoids, and the Cu atoms are shown as blue ellipsoids with principal ellipses. The unit cell is outlined.

Our interest in the low-temperature properties of various uranium-containing intermetallics, coupled with systematic syntheses employing flux-growth techniques (Canfield & Fisk, 1992), led us to the discovery of a previously unnoticed phase width in the title compound. This effect is clearly seen in the refined site occupancies, but can also be inferred from the difference in the unit-cell parameter  $c$  [20.317 (2) Å at 120 K, this work], which is almost 0.05 Å longer than at room temperature [ $c = 20.271$  (4) Å; Stepien-Damm *et al.*, 1999].

Additional evidence in support of the observed stoichiometry width in  $\text{UCu}_{5-x}\text{Sn}$  can also be found upon comparison of the isotropic displacement parameters of the Cu atoms; the value for one of the Cu sites is about 75% smaller than those of the remaining Cu atoms (Stepien-Damm *et al.*, 1999). A similar anomaly is evident from the structure refinement of  $\text{UCu}_5\text{Sn}$  from neutron data (Tran *et al.*, 1999), with a reported  $c$  axis of 20.2944 (9) Å, more than 0.02 Å different from the previously reported value (Stepien-Damm *et al.*, 1999). All of the above suggests that the early reports on  $\text{UCu}_5\text{Sn}$  might have overlooked potential partial occupancy or disorder on two Cu sites, *viz.* Cu1 (Wyckoff 12k) and Cu3 (Wyckoff 2c).

The structure of  $\text{UCu}_{5-x}\text{Sn}$  can be viewed as being made up of large polyhedral cages of Cu and Sn, centred by U atoms [U1 with coordination number (CN) of 20, U2 with CN of 18; Fig. 1]. Important structural features have previously been described in detail (Stepien-Damm *et al.*, 1999; Villars & Calvert, 1991) and will therefore not be given further consideration here. It is worthwhile pointing out that the structure is topologically similar to that of the orthorhombic  $\text{RECu}_{6-x}\text{In}_{1-x}$  phases ( $\text{RE} = \text{rare-earth metal}$ ), in which Cu/In are disordered (Bobev & Bauer, 2005). The possibility of statistical disorder of Cu and Sn in  $\text{UCu}_{5-x}\text{Sn}$  on any of the Cu and Sn sites was evaluated in the present refinements, but ruled out. This supports the findings of Tran *et al.* (1999) and confirms the conclusion that two of the Cu sites are indeed partially occupied. Most likely, the different synthetic techniques – flux growth (present study) *versus* arc-melting and annealing (all previous studies) – explain the subtle differences in the cell volumes and compositions.

## Experimental

A mixture of the reactants, in a stoichiometric ratio U:Cu:Sn = 1:5:2, 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 1373 K for 4 h, and cooled at 3 K h<sup>-1</sup> to 1073 K, whereupon it was removed from the furnace. The excess of the molten Cu–Sn eutectic solution was removed by centrifugation.

### Crystal data

$\text{UCu}_{4.63}\text{Sn}$   
 $M_r = 650.59$   
 Hexagonal,  $P6_3/mmc$   
 $a = 4.9855$  (3) Å  
 $c = 20.317$  (2) Å  
 $V = 437.32$  (6) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 9.881$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 3213 reflections  
 $\theta = 2\text{--}28^\circ$   
 $\mu = 64.36$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Irregular fragment, grey  
 0.10 × 0.05 × 0.04 mm

### Data collection

Bruker SMART APEX diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)  
 $T_{\min} = 0.027$ ,  $T_{\max} = 0.076$   
 3213 measured reflections

254 independent reflections  
 225 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$   
 $\theta_{\max} = 28.2^\circ$   
 $h = -6 \rightarrow 6$   
 $k = -6 \rightarrow 6$   
 $l = -23 \rightarrow 27$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.079$   
 $S = 1.17$   
 254 reflections  
 24 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.4422P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 2.82$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -2.07$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0068 (8)

**Table 1**

Selected bond lengths (Å).

|                       |              |                         |              |
|-----------------------|--------------|-------------------------|--------------|
| U1—Cu3 <sup>i</sup>   | 2.87836 (17) | Cu1—Cu1 <sup>viii</sup> | 2.483 (3)    |
| U1—Cu4 <sup>ii</sup>  | 2.87838 (17) | Cu1—Cu1 <sup>ix</sup>   | 2.503 (3)    |
| U1—Cu1 <sup>iii</sup> | 3.2516 (9)   | Cu1—Cu4                 | 2.5324 (14)  |
| U2—Cu2 <sup>iv</sup>  | 3.0164 (7)   | Cu1—Cu2                 | 2.540 (2)    |
| U2—Cu1                | 3.3172 (14)  | Cu2—Cu1 <sup>x</sup>    | 2.540 (2)    |
| Sn—Cu2 <sup>v</sup>   | 2.620 (3)    | Cu3—Cu1 <sup>xi</sup>   | 2.5390 (15)  |
| Sn—Cu1 <sup>vi</sup>  | 2.7990 (10)  | Cu3—Cu4 <sup>xii</sup>  | 2.87838 (17) |
| Sn—Cu2 <sup>vii</sup> | 2.9919 (8)   |                         |              |

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

Initial refinements assuming a fully stoichiometric formula led to convergence with very good residuals, yet two of the Cu sites had significantly smaller displacement parameters than the rest. Refinements by freeing the site occupation factor for an individual atom, while other remaining parameters were kept fixed, proved that Cu1 is 89.6 (8)% occupied while Cu3 is 88 (1)% occupied, which leads to the formula  $\text{UCu}_{4.63(1)}\text{Sn}$ . The occupancy factors for all other sites did not deviate from full upon free refinement (variations 98 to 102%). The maximum peak and deepest hole are located 0.75 Å from U2 and 0.13 Å from Sn, respectively. Note: the coordinates reported here are those obtained after standardization using the program *STRUCTURE TIDY* (Gelato & Parthe, 1987). This shifts the origin by (0, 0,  $\frac{1}{2}$ ) and interchanges the labels of some of the atoms: Cu1, Cu2, Cu3 and Cu4 in the refinement of Stepien-Damm *et al.* (1999) become Cu4, Cu1, Cu2, and Cu3, respectively. Comparison of the labels and the coordinates for  $\text{UCu}_5\text{Sn}$  (Stepien-Damm *et al.*, 1999) and the archetype  $\text{CeNi}_5\text{Sn}$  (Villars & Calvert, 1991) shows discrepancies, although  $\text{UCu}_5\text{Sn}$  is explicitly stated to be with the  $\text{CeNi}_5\text{Sn}$ -type. Therefore, *STRUCTURE TIDY* (Gelato & Parthe, 1987) was used to standardize the coordinates and to eliminate future problems with reporting and referencing compounds with this structure.

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*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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