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## CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE OF $UCu_{1.5}Sn_2$

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### Abstract

We report on the crystallographic and magnetic structures of the antiferromagnet  $UCu_{1.5}Sn_2$ , as determined by x-ray and neutron powder diffraction. It forms in the tetragonal  $CaBe_2Ge_2$  structure type, with space group  $P/4nmm$ , and we find no site disorder between two different Sn 2c sites, in contrast with a previous report.  $UCu_{1.5}Sn_2$  orders antiferromagnetically with a Néel temperature of about 110 K. This is unusually high amongst uranium intermetallics. The uranium moments align along the c-axis in a collinear arrangement but alternating along the c-axis. The low-temperature uranium moment is  $1.95\mu_B$ .

### 1. Introduction

In the last decade many studies have been performed on the large family of tetragonal Ce- and U-based ternary intermetallic compounds with stoichiometry  $CeT_2X_2$  or  $UT_2X_2$  (T = transition metal; X = Group IV element), with a view to understanding their magnetic and/or heavy-fermion properties<sup>1</sup>. Those compounds with X = Si or Ge have been studied most extensively, and they include the celebrated heavy-fermion superconductors  $CeCu_2Si_2$  and  $URu_2Si_2$ . Most such compounds form in the body-centred tetragonal  $ThCr_2Si_2$  structure (space group  $I4/mmm$ ), though a significant minority form in the closely related primitive tetragonal  $CaBe_2Ge_2$  structure (space group  $P4/nmm$ ). In some cases, like  $UCo_2Ge_2$ , both forms can be produced depending on the heat treatment and stoichiometry of the sample<sup>2</sup>. The difference between the two structures is

in the stacking sequence of the T and X layers between the layers of Ce or U atoms, as one progresses along the tetragonal axis.

We have recently started to work on  $UT_2Sn_2$  compounds, and in this article we report on the crystallographic and magnetic properties of the antiferromagnet  $UCu_2Sn_2$ , as studied by X-ray and neutron diffraction.  $UCu_2Sn_2$  is remarkable amongst uranium intermetallics for having a Néel temperature above 100K, while it is more typical for uranium compounds (without Co or Fe) to order magnetically at 50K or below, if at all.  $UCu_2Sn_2$  with a slight copper deficiency had previously been studied by means of X-ray diffraction by Pöttgen et al.<sup>4</sup>, and these authors found the  $CaBe_2Ge_2$  structure type, but with 2 interesting features. Firstly, in the stoichiometry  $UCu_{1.3}Sn_2$ , they found the copper deficiency to be entirely located on the 2c-type sites, as shown in Fig. 1(a). Secondly, regarding the tin atoms on the 2c-type sites in the other half of the unit cell, they found it necessary to use two such sites with significantly different z-parameters. Again, this is shown schematically in Fig. 1(a). We have repeated their study on a sample with slightly less copper deficiency using both X-ray and neutron diffraction. While we find the same sort of copper deficiency on the copper 2c-sites, we do not have to invoke the bimodal distribution of Sn atoms over two different sites with different z-parameters. In addition, we have used our neutron diffraction data to determine the magnetic structure, the magnitude of the uranium moment and to estimate the Néel temperature.

## 2. Experimental Method

The polycrystalline sample was prepared by arc melting stoichiometric amounts of the constituent elements of at least 9.99% purity. The phase purity was checked by powder X-ray diffraction using  $CuK\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), and the X-ray data were analysed using the Rietveld refinement program GSAS<sup>4</sup>. A very small amount of impurity scattering was observed. For the neutron experiment, the  $UCu_2Sn_2$  powder was sealed in vanadium tube under a helium

atmosphere, and this was in turn mounted in a helium cryostat. The cryostat was mounted on the C5 powder diffractometer, at the Chalk River Laboratory, in such a way that it could be rotated continuously to give a better powder average over the grains in the sample. A rotating collimator was also used, between sample and the large area detector, to eliminate background peaks from the cryostat tails. We used a Si (531) monochromator with a wavelength of 1.51Å, and data were recorded between 5° and 85° (for the magnetic scattering) and between 41° and 121° (for the structural analysis). Data were taken at a variety of temperatures between 6 K and 120K, and they were analysed both by Rietveld refinement using GSAS<sup>4</sup>, as well as by peak-by-peak extraction of integrated intensities for the magnetic structure.

### 3. Results

The results of the Rietveld refinements using our X-ray and neutron data are listed in Table 1. We obtain a good refinement using the CaBe<sub>2</sub>Ge<sub>2</sub> structure. Secondly, we find a copper deficiency on the Cu 2c-site, as found before by Pöttgen et al.<sup>4</sup>, and we deduce a stoichiometry close to UCu<sub>1.5</sub>Sn<sub>2</sub>, i.e. slightly less copper deficient than Pöttgen's sample. However, in contrast with their results, we find no need to invoke two different Sn 2c-sites. Not only does Pöttgen's model give a worse  $\chi^2$  than the model with a single z-value for the Sn 2c-site, but if the occupancies on the two sites are allowed to vary in the refinement, it converges to 100% on the one site and 0% on the other. We therefore believe that our sample has the structure listed in Table 1 and shown in Fig. 1 (b).

Regarding the magnetic structure, some of our low-angle neutron diffraction data are shown in Fig. 2. Three extra peaks, indexed as 010, 012 and 111, are seen at low temperature. We presume that these are magnetic and also note that no extra intensity is seen at the (001), (002), or (110) positions, which would also fall in this angular range. The fact that the observed reflections have no fractional indices implies that the magnetic cell is probably the same as the crystallographic cell,

and that there are only two uranium atoms per magnetic cell. If we ignore the Cu and Sn ions, the two uranium atoms lie on a body-centred tetragonal lattice, and the fact that the magnetic reflections obey the  $h+k+l = 2n + 1$  selection rule implies that the two uranium moments are antiparallel to each other. In addition, the fact that no (001) reflection is seen implies that the moments must be parallel to the c-axis, giving the simple collinear antiferromagnetic structure shown in Fig. 3. As it happens, a Shubnikov-group analysis of the 2c-sites (point group 4mm) shows that this is one of two allowed magnetic extensions to P4/nmm: the other would be a simple c-axis ferromagnet, which would only contribute extra magnetic intensity to the existing nuclear reflections. Fitting this model to our data yields a low-temperature uranium moment of  $1.61 \pm 0.01 \mu_B$ . A comparison of the observed and calculated magnetic intensities is given in Table 2.

Finally, the intensities of all three magnetic reflections are shown in reduced units, as a function of temperature, in Fig. 3 along with a fitted Brillouin function. This yields a transition temperature of  $T_N = 107 \pm 27K$ .

#### 4. Discussion

A large number of uranium-based intermetallic antiferromagnets have now been studied in a variety of cubic, hexagonal and orthorhombic structures<sup>6</sup>. Almost invariably, these materials show strong magnetic anisotropies, with the moments aligned perpendicular to planes or chains defined by nearest-neighbour uranium-uranium links. The physical rationale for this is that the f moments are hybridised more strongly, with ligand p and d electrons, in these directions or planes. They can better support "localised" moments in the directions of weaker hybridisation, which are necessarily perpendicular. A second observation is that the coupling within the strongly hybridised planes or chains is usually ferromagnetic. This picture has also recently been shown to apply in several tetragonal  $U_2T_2X$  ( $X = In, Sn$ ) compounds<sup>6</sup>. It is instructive to apply this idea in the

present case: in  $\text{UCu}_{1.5}\text{Sn}_2$ , the nearest-neighbour U-U distance,  $d_{\text{U-U}}$  in Fig. 1(c), lies in the tetragonal basal plane along the **a** and **b** directions, with a length  $a = 4.39\text{\AA}$ . This is significantly greater than the Hill limit of  $3.5\text{\AA}$ , beyond which localised uranium moments might be expected. It also implies that these ordered moments should align perpendicular to the tetragonal basal plane, i.e. along the **c**-axis. This is exactly what we observe. In addition, the moments are also ferromagnetically coupled within the tetragonal sheets, in agreement with the phenomenology in other uranium intermetallics.

In summary, we have shown definitively that  $\text{UCu}_{1.5}\text{Sn}_2$  orders into a simple collinear **c**-axis antiferromagnetic structure below 100K, with a low-temperature uranium moment of  $1.95 \mu_{\text{B}}$ . This is quite large, indicating fairly localised moments, though still well short of the full Hund's rule moment which would be in excess of  $3\mu_{\text{B}}$ . We also find the copper deficiency on the 2c-type sites in agreement with Pöttgen et al., but find no evidence for a bimodal distribution of Sn atoms on different 2c-type sites with different **z**-parameters.

### Acknowledgements

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## Figure Captions

- Figure 1 Schematic diagrams of the structure of  $\text{UCu}_{1.5}\text{Sn}_2$ , as reported (a) by Pöttgen et al. (see Ref. 4), and (b,c) in this work. In all cases the tetragonal c-axis is shown as vertical. The atomic occupancies are shown in the projection onto the a-c plane in (c), with the partially filled Cu 2c-sites shown by the open circles, while the fully occupied Cu 2a-sites are represented by filled circles. The closest U-U distance  $d_{\text{U-U}}$  is also shown in (c), while the collinear c-axis antiferromagnetic structure reported in the text is shown in both (b) and (c). The bimodal distribution of Sn atoms over two different z-parameter 2c-sites reported by Pöttgen et al., but not seen in our work, is shown by the dumbbells in (a). The origin in this figure corresponds to (0.25, 0.25, 0.25) in the coordinates given in Table 1.
- Figure 2 Low-angle neutron diffraction patterns taken at (a) 120K, (b) 6K and (c) the difference between 6K and 120K. Note that three magnetic peaks (010), (012) and (111) are observed, but that there is no magnetic contribution to the (001), (002) or (110) nuclear reflections.
- Figure 3 Variation of the reduced intensity of the (010), (012) and (111) magnetic reflections. The solid line shows a fitted Brillouin function, with  $T_N = 107\text{K}$ .

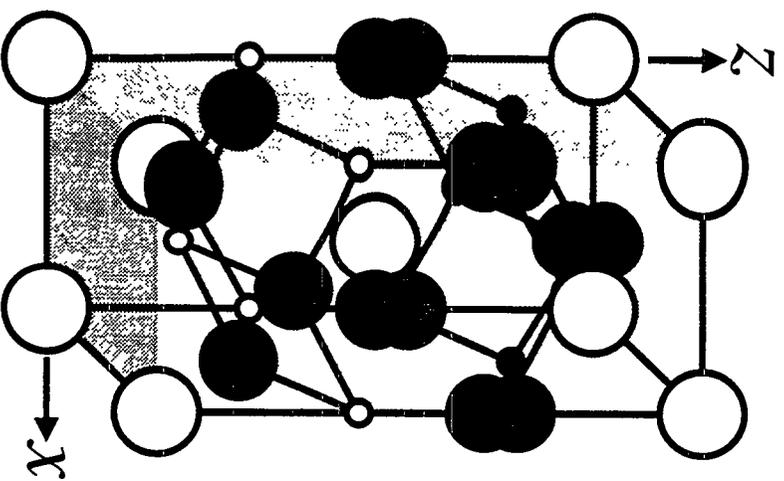
Table I: Refined Structural Parameters for  $\text{UCu}_{1.5}\text{Sn}_2$  at room temperature (X-ray) and at 120 K (neutron).

				Space Group P4/nmm	% occupancy	
U(2c)	0.25	0.25	z	$z = 0.2400 \pm 0.0006$ $z = 0.2435 \pm 0.0004$	100 100	(neutron) (X-ray)
Cu(2c)	0.25	0.25	z	$z = 0.6137 \pm 0.0012$ $z = 0.6004 \pm 0.0021$	$45.1 \pm 1.9$ $58.1 \pm 2.7$	(neutron) (X-ray)
Cu(2a)	0.75	0.25	0		$107.6 \pm 2.1$ $104.3 \pm 3.4$	(neutron) (X-ray)
Sn(2b)	0.75	0.25	0.5		$103.7 \pm 2.4$ $100.0 \pm 1.7$	(neutron) (X-ray)
Sn(2c)	0.25	0.25	z	$z = 0.8415 \pm 0.0006$ $z = 0.8472 \pm 0.0006$	$95.6 \pm 2.8$ $101.5 \pm 1.3$	(neutron) (X-ray)
Lattice Constants ( $\text{\AA}$ )					$a = 4.3858 \pm 0.0003$ $a = 4.3920 \pm 0.0002$	(neutron) (X-ray)
					$c = 9.6412 \pm 0.0007$ $c = 9.6480 \pm 0.0004$	(neutron) (X-ray)
R factors (%)					$R_{\text{wp}} = 11.06$ $R_{\text{wp}} = 14.52$ $R_{\text{p}} = 8.50$ $R_{\text{p}} = 11.12$	(neutron) (X-ray) (neutron) (X-ray)
					Reduced $\chi^2 = 7.821$ Reduced $\chi^2 = 2.163$	(neutron) (X-ray)

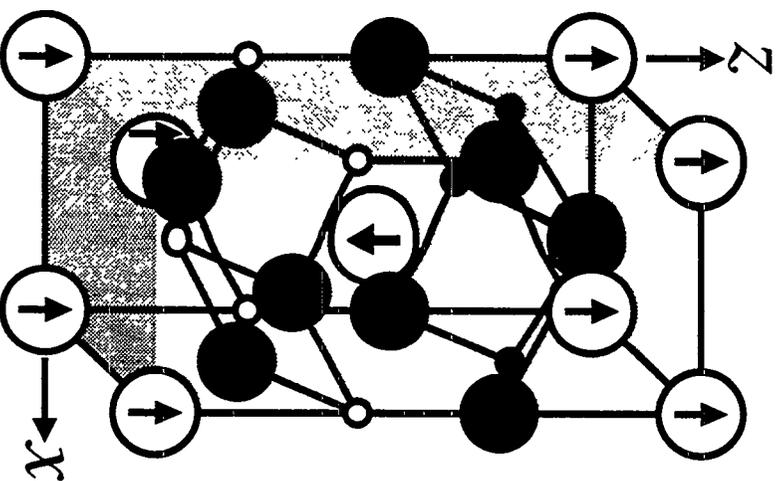
Table II Observed and Calculated Intensities for Magnetic Reflections in  $\text{UCu}_{1.5}\text{Sn}_2$

Reflection	Observed Intensity	Calculated Intensity
010	$10.87 \pm 0.26$	10.94
012	$10.51 \pm 0.58$	10.55
111	$16.96 \pm 0.56$	16.69

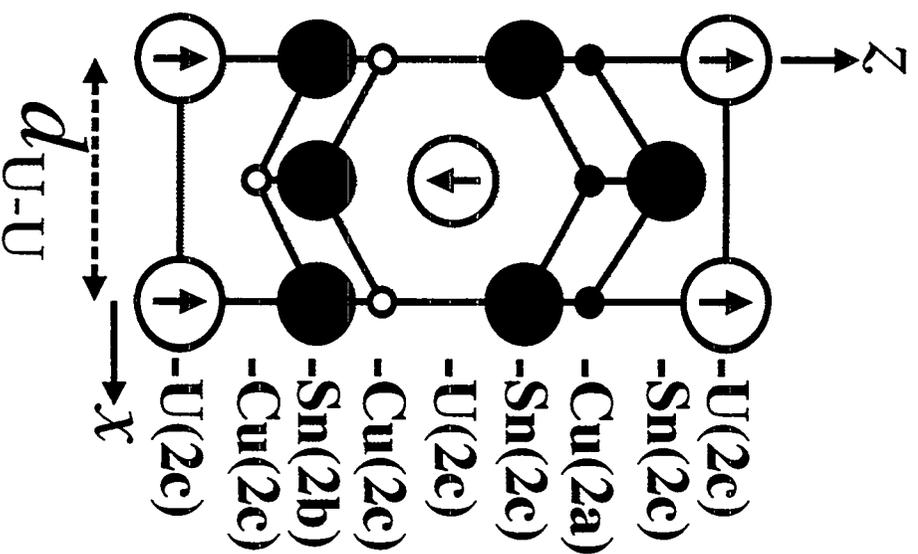
Reduced  $\chi^2 = 0.4$



(a)



(b)



(c)

