Crystallographic and magnetic properties of UAuSn

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The uranium intermetallic compound UAuSn has been studied by means of neutron powder diffraction. It crystallizes in the $CaIn_2$ structure type, with space group $P6_3/mmc$, in agreement with previous x-ray work. Below 37 K, it exhibits long-range antiferromagnetic order, in a double-sized orthohexagonal magnetic unit cell. At the lowest temperature measured, the uranium moment is $1.10\mu_B$. The magnetic structure is collinear with moments parallel to the orthorhombic b axis and the magnetic space group is $C_pm'cm'$. We discuss the Au/Sn disorder in terms of metallic radii and discuss the consequences of this symmetry on the collinearity of the magnetic structure. These results are compared with work on the isostructural compounds UPdSn and UCuSn.

I. INTRODUCTION

Ternary uranium intermetallic compounds UTX, of composition 1:1:1, have been studied extensively in order to get insight into the role of $5f$-d hybridization in the formation of the uranium magnetic moment. This hybridization is critically dependent on the choice of elements T and X, in the case of compounds crystallizing in the same structure. In this article, we report on UAuSn which crystallizes in the $CaIn_2$ structure type, with space group $P6_3/mmc$ and orders antiferromagnetically at approximated 36 K.[1,2] Other compounds crystallizing in this or related structures are UPdSn, UPdSb, and UCuSn. Of these, UPdSn has been studied most extensively by means of the full range of bulk techniques[1,2] as well as neutron diffraction[3-6] and photoemission.[7] It was found to exhibit ordering of the Pd and Sn atoms; they should be randomly distributed over the "In" sites in the $CaIn_2$ structure. This ordered version of the $CaIn_2$ structure type is the noncentric GaGeLi structure type, with space group $P6_3mc$. UPdSn was also found to exhibit a fairly complicated canted antiferromagnetic structure with a second phase transition at low temperature to a yet more complicated noncollinear antiferromagnetic structure. These magnetic structures and transitions can be understood in terms of a normal magnetic space group analysis, provided that the structural space group is $P6_3mc$. In contrast, the x-ray diffraction data on UAuSn

(Ref. 2) indicate that the Au and Sn atoms are indeed randomly distributed over the "In" sites of the $CaIn_2$ structure. Although the magnetic susceptibility of UAuSn is qualitatively similar to that of UPdSn,[1] the specific-heat and Mössbauer results have led to speculation that UAuSn does not exhibit long-range magnetic order at all.[2] In order to resolve this question, we have made neutron powder-diffraction measurements on UAuSn and demonstrate that it does indeed exhibit long-range collinear antiferromagnetic order, with a uranium moment of $1.10\pm0.02\mu_B$. We also confirm the x-ray result regarding the Au/Sn ordering and discuss the observed magnetic structure in terms of this symmetry.

II. EXPERIMENTAL METHOD

The sample was prepared as reported previously[1] by arc melting the constituent elements of at least 99.9% purity under argon gas. After arc melting, the sample was wrapped in Ta foil and vacuum annealed at 800 °C for 3 weeks. X-ray diffraction analysis of the sample indicates the presence of some USn_3, in addition to the main UAuSn phase. 8.0 g of sample were ground and enclosed in a sealed vanadium tube. This in turn was sealed in an aluminum tube and mounted in a computer-controlled closed-cycle refrigerator, which was mounted on the neutron diffractometer. Full diffraction patterns were mea-
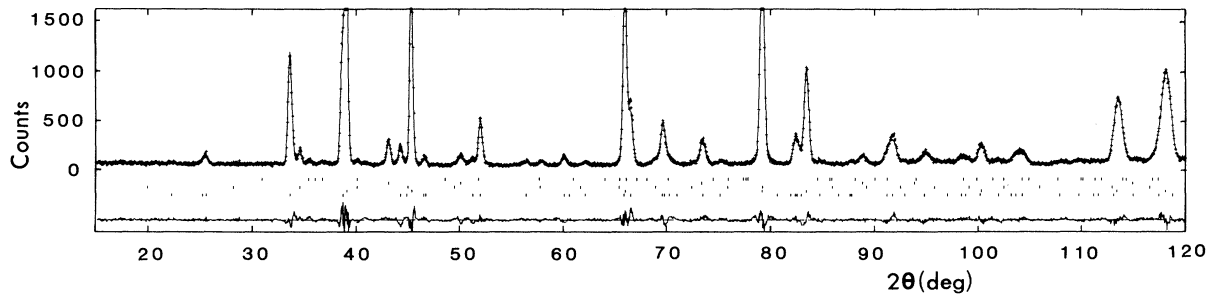
FIG. 1. Observed data and calculated nuclear structure profiles for UAuSn at 60 K, as measured on BT-1 at NIST. Starting from the bottom, the reflection markers indicate UAuSn, aluminum (can), USn_3, stainless steel, and α-U.

sured at 60 K and 9 K on the BT-1 powder diffractometer at the NIST Research Reactor, using a wavelength of 1.545 Å and scattering angles between 5° and 120°. Further low-resolution measurements were made on the BT-2 triple-axis spectrometer in two-axis mode, with a vertically focusing pyrolytic graphite monochromator and graphite filter. In this case, the wavelength was 2.35 Å, the collimation was 60′/60′/60′ and scans were made between scattering angles of 5° and 65°. The relatively coarse resolution was chosen to maximize the integrated intensity in the magnetic reflections, which were barely visible in the BT-1 run.

III. RESULTS

Figure 1 shows the full data set measured on BT-1 at 60 K. Rietveld refinement has been performed using the Generalized crystal Structure Analysis System (GSAS)

program,[8] which allows simultaneous refinement of multiple phases. Three sample phases were refined, UAuSn, USn_3 (Ref. 9) and α-U (Ref. 9), along with the aluminum pattern from the sample can and an FCC pattern, presumably from the stainless-steel sample cap of the vanadium can, which had not been completely shielded with cadmium. Because of the strong preferred orientation in the aluminum pattern, and the fact that it is several times more intense than the UAuSn pattern, we used Le Bail's method for the aluminium peaks. The patterns were refined using both $CaIn_2$ ($P6_3/mmc$) and GaGeLi ($P6_3mc$) structures for UAuSn and the refinements clearly indicate that the space group is the former, in agreement with recent x-ray results.[2] The reduced χ^2 is 60% greater when one assumes the GaGeLi structure. The parameters obtained from the refinement are listed in Table I and are in very good agreement with the x-ray results of de Boer et al.[2]

TABLE I. Refined structural parameters for UAuSn.

Space Group $P6_3/mmc$

U	$2b$	0	0	1/4	
Au/Sn	$4f$	1/3	2/3	z	$z = 0.4583 \pm 0.0003$

Lattice parameters

60 K	9 K
a (Å) 4.711652±0.00043	a (Å) 4.71521±0.00045
c (Å) 7.20347±0.00086	c (Å) 7.19865±0.00089

c/a ratio	1.5273
Nearest-neighbor U-U distance	3.602 Å
Next-nearest-neighbor U-U distance	4.171 Å

Other phases in Fig. 1:

Aluminum (sample can)
USn_3 (space group $Pm\bar{3}m$)   9.7% of sample by volume
FCC iron (part of stainless-steel cap to can)
α-U (space group $CmCm$)   0.7% of sample by volume

R factors

$R_{wp} = 11.41\%$
$R_p = 8.34\%$
Reduced $\chi^2 = 2.25$

Low resolution scans were also made on BT-2. Figure 2 shows the high-temperature data subtracted from the data taken at 11 K, in the magnetically ordered state. These initial scans were counted for one minute per point, and clearly reveal magnetic Bragg peaks at 29.0°, 41.9°, and 48.7°. These angular ranges were then counted for an additional four minutes per point at each temperature to improve the counting statistics, and the data have been fitted to these three peaks plus "background." Note that in this case the "background" is slightly negative, which is because the diffuse magnetic paramagnetic scattering at high temperature has moved into the magnetic Bragg peaks. A discussion of this subtraction procedure to isolate the magnetic Bragg peaks is given in Ref. 10. The observed magnetic peaks can be indexed in a double-sized orthorhombic unit cell as the (100), (012), and (102) reflections. Note that there are no reflections with l odd, in contrast to the situation in UPdSn where the (011) and (101) reflections were observed.[3,4] Furthermore, the (010) reflection at 16.5° is absent and the (120) reflection which should be at 44.8° is very weak.

Following the analysis of Ref. 3, it is clear that the $l = 2n$ selection rule can be met by a collinear structure in which the atoms at $(0,0,\pm1/4)$ are polarized antiparallel to those at $(1/2,1/2,\pm1/4)$. Neglecting the Debye-Waller factor and magnetic form factor, the intensity of a magnetic Bragg reflection with indices hkl is proportional to

$$I_{hkl} = 16\mu^2\sin^2\eta \cos^2\left\{\frac{\pi l}{2}\right\}\sin^2\left\{\frac{\pi(h+k)}{2}\right\}, \quad (1)$$

where μ is the uranium moment, and η is the angle between the moment direction and the reciprocal lattice vector for that Bragg reflection. This expression gives the selection rules that l must be even and that $(h+k)$ must be odd. As for the moment direction, the fact that no intensity is seen in the (010) reflection indicates that the moments must be parallel to the orthorhombic b axis. This magnetic structure is shown in Fig. 3, and it has symmetry $C_p m'cm'$, in Prandl's notation.[11] After

FIG. 3. Projection of the magnetic structure of UAuSn on to the hexagonal basal plane. For the sake of clarity, only the uranium atoms are shown. The orthorhombic cell is denoted by solid lines, with the atoms at $(0,0,\pm1/4)$ polarized antiparallel to those at $(1/2,1/2,\pm1/4)$. The hexagonal cell is shown by the dashed lines.

correcting for the Lorentz factor[12] and for the uranium magnetic form factor,[13] a reasonable fit to the observed magnetic intensities is achieved. We obtain a moment of $1.10\pm0.02\mu_B$, with a reduced χ^2 of 2.5. The observed and calculated integrated intensities are listed in Table II.

The temperature variation of peak intensity of the (100) reflection was also measured and the data are shown in Fig. 4. No significant hysteresis was observed on heating and cooling. They have been fitted to a Brillouin function and the resultant Néel temperature is 37 ± 1 K, which is in good agreement with the bulk measurements.[1,2] This is clear evidence of the magnetic origin of these extra peaks.

IV. DISCUSSION

Qualitatively, the fact that the Au/Sn atoms are crystallographically disordered in UAuSn while the Pd/Sn atoms are ordered in UPdSn can be understood in terms of the relative differences in atomic radius. The metallic radii of Au and Sn differ by between 7% and 12.5% de-
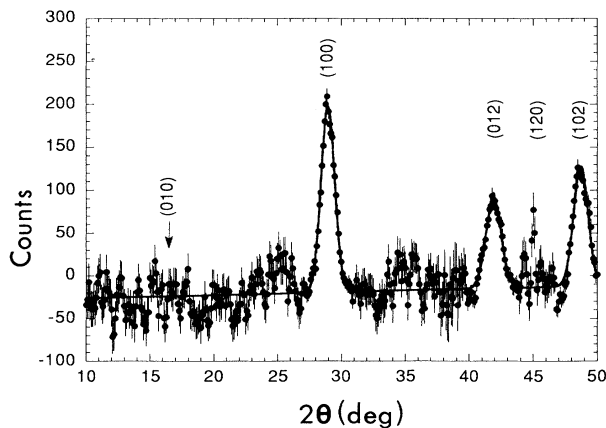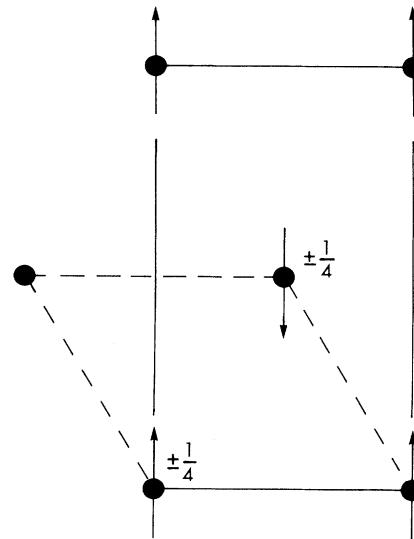

FIG. 2. Difference plot (11–50 K) of intensity measured on BT-2 at NIST. The data were counted at 5 minutes per point. Note the absence of the (010) magnetic reflection at 16.5°.

TABLE II. Indexing and intensities of magnetic reflections in UAuSn at low temperature.

Orthorhombic indices	2θ	Observed intensity at 11 K[a]	Calculated intensity[a]
010	16.5°	0.0000±0.000 1	0
100	29.0°	0.0070±0.000 3	0.0066
012	41.9°	0.0080±0.000 6	0.0099
120	44.8°	0.0027±0.000 9	0.0049
102	48.7°	0.0136±0.001 1	0.0109

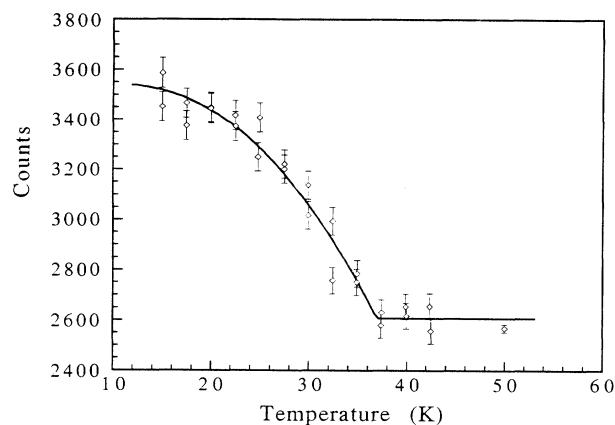[a]$I_{hkl}\sin\theta_{hkl}\sin(2\theta_{hkl})/[I_{112}\theta_{112}\sin(2\theta_{112})]$.

FIG. 4. The variation of peak intensity of the (100) magnetic reflection in UAuSn, measured on BT-2 at NIST. The solid line is to fit to a Brillouin function and it gives a Néel temperature of $T_N = 37 \pm 1$ K.

pending on the valence of Sn, while those of Pd and Sn differ by 12.2% to 18%.[14] The well-known empirical rule of Hume-Rothery and co-workers[15] indicates a solid solution to be likely if the relevant atomic radii differ by less than 15%. So UAuSn is more likely to be disordered than UPdSn. Furthermore, the c/a ratios for UAuSn and UPdSn are quite different: UPdSn is stretched in the c direction, but contracted within the hexagonal plane. Similar atomic radius arguments indicate that UCuSn should be ordered, and the c/a ratio is indeed more extreme than that of UPdSn.

If a Landau theory can be applied to the magnetic transition, that is if the transition is second order or nearly so, then a magnetic space group analysis can be applied. In fact our case, $P6_3/mmc$ or in the orthorhombic magnetic cell $Cmcm$, has already been tabulated by Prandl.[11] He shows that in all possible magnetic structures, the uranium moments on the $(0,0,\pm 1/4)$ sites must be collinear, which is indeed what we observe in UAuSn. Our data show that the moments are aligned along the orthorhombic b axis and that the magnetic space group is $C_p m'cm'$, in Prandl's notation.[11] However, if the Au and Sn atoms were chemically ordered, then a mirror plane is lost (along with inversion symmetry) and the crystallographic space group would then be $P6_3mc$. Canting of the magnetic moments would then be

allowed. This is what occurs in UPdSn, where the Pd and Sn atoms are indeed ordered crystallographically, for the reasons discussed in the previous paragraph, and the first magnetic transition is to a state with noncollinear moments confined to the b-c plane.[3] A possible mechanism for the canting would be the Dzyaloshinskii-Moriya interaction[16] which can occur in noncentric groups, but which is absent by symmetry in groups with inversion symmetry. It is also instructive to consider the case of UCuSn which, if it is ordered crystallographically, would also be expected to exhibit such noncollinear magnetic order. Recent neutron diffraction data due to Fujii[17] on a multiphase sample of UCuSn do indeed exhibit $l = 1$ magnetic diffraction peaks that are indicative of noncollinearity.

The magnetic anisotropy of UPdSn is very unusual. Although the c axis is in some sense the hard axis,[2,4] the moments do not lie completely in the hexagonal basal plane. Indeed, the angle of inclination to the c axis is almost temperature independent indicating that this degree of freedom is very stiff. It is difficult to understand this observation in any simple local-moment model. In contrast, in UAuSn the moments lie in the hexagonal basal plane and it would be of interest to determine its anisotropy by bulk measurements on a single crystal, in order to determine whether the unusual anisotropy of UPdSn is a consequence of the noncentric nature of the crystallographic space group.

Our moment of $1.10\mu_B$ is significantly less than the extrapolated high-field saturation values, which are in excess of $1.6\mu_B$, though these values are not yet reached even at fields of $35T$.[2] It may be that this discrepancy lies in the band nature of the magnetism in UAuSn, when compared with UPdSn which seems to be more localized in character. Not only are the moments smaller in UAuSn, but the specific-heat coefficient γ is at least an order of magnitude larger.

ACKNOWLEDGMENTS

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