Crystallographic and magnetic properties of UPdSn

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A single crystal of the intermetallic compound UPdSn has been studied by means of neutron diffraction using the white-beam Laue diffractometer (single-crystal diffractometer) at the Los Alamos spallation neutron source. Data were taken in the paramagnetic phase at 55 K and just below the Néel point at 37 K. The crystallographic data refine well within the space group $P6_3mc$ and confirm the results obtained previously on powders, namely that the Pd and Sn atoms are ordered. At low temperature, UPdSn undergoes two phase transitions at 40 and 25 K to complicated noncollinear antiferromagnetic structures. All three pairs of magnetic domains are observed, in roughly equal populations, in the intermediate-temperature orthorhombic magnetic structure (phase I). A uranium moment of $0.863\mu_B$ and canting angles $\phi = 56.51°$ and $\theta = 21.42°$ were obtained, in reasonable agreement with previous powder neutron data for this temperature. The observed form factor yields an orbital-to-spin moment ratio $-\mu_L/\mu_S = 2.6$ which is characteristic of the trivalent f^3 configuration.

I. INTRODUCTION

The noncollinear antiferromagnet UPdSn is one of the set of uranium (1:1:1) ternary intermetallic compounds[1] that is being studied with a view to understanding the role of $5f$-d hybridization in uranium moment formation. It is also of interest in that the magnetic atoms lie on a simple hexagonal lattice, and yet it exhibits a strange and complicated type of magnetic order, which must be indicative of a bizarre magnetic anisotropy. Previous powder studies have clarified the crystallographic structure,[2,3] which is the GaGeLi structure type with space group $P6_3mc$. They have also shown the presence of antiferromagnetic order at low temperatures, with a Néel point at approximately 40 K, and a second phase transition at approximately 25 K. Between 25 and 40 K, UPdSn is a canted antiferromagnet with two order parameters μ_y and μ_z in the orthorhombic cell, while below 25 K a third component of the moment μ_x develops. Alternatively, using the spherical-polar canting angles defined in Fig. 1, $\theta = 0$ in phase I. In this article we report single-crystal measurements made just above and below the Néel point, at 55 and 37 K, respectively.

II. EXPERIMENTAL METHOD

The crystal was grown by the tri-arc Czochralski method, and has a cylindrical form with a diameter of approximately 1 mm and a length of 5 mm. The cylinder axis was approximately 18° away from the crystallographic $[1\bar{1}0]_{\text{hexagonal}}$ ($= [100]_{\text{orthorhombic}}$) axis. It was glued on to an aluminum-alloy pin, which was attached to the cold finger of a closed-cycle helium refrigerator. This refrigerator is an integral part of the single-crystal diffractometer (SCD),[4] which is essentially a time-of-flight Laue camera, at the pulsed spallation neutron source at Los Alamos.

III. RESULTS AND DISCUSSION

We collected complete sets of data in both the paramagnetic and intermediate-temperature phases (magnetic phase I), at 55 and 37 K, respectively. The crystallographic structure refines well to $P6_3mc$, with the parameters listed in Table I. These numbers are in good agreement with previous neutron powder and single-crystal x-ray work,[2,5] but as in the powder work, the scattering-length contrast is such that we cannot tell which of Pd and Sn is on which sites. However, it is clear that there are two crystallographically distinct sites, and we presume that the Pd and Sn atoms are ordered, with Sn on the site with more room. This structure is shown in Fig. 1.

As for the magnetic scattering, all three pairs of domains were observed, and at least 70 magnetic reflections
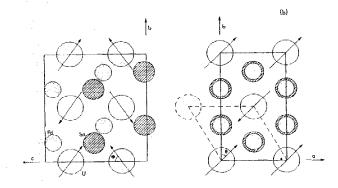

FIG. 1. The magnetic structure of UPdSn at low temperature (magnetic space group P_c2_1), projected on to the b-c and a-b planes, respectively. The cell shown is the orthorhombic magnetic unit cell, with two uranium layers per unit cell. Note that this structure exhibits c-side anticentering. At low temperature (magnetic phase II of Ref. 2), $\phi = 54°$ and $\theta = 45°$. In magnetic phase I (40 K $> T > 25$ K), $\theta = 0°$ but ϕ retains the value of 54°. The hexagonal unit cell is shown by the dashed lines.

TABLE I. Refined structural parameters for UPdSn at 55 K.

Space Group				$P6_3mc$	
U	2a	0	0	z	$z=1/4$ (fixed to define origin)
Pd	2b	1/3	2/3	z	$z=0.4225\pm0.0012$
Sn	2b	2/3	1/3	z	$z=0.5181\pm0.0015$

a (Å) 4.611 ± 0.006
c (Å) 7.261 ± 0.050

R factors:
$R_w=5.4\%$ ($R_w=9.1\%$ if refined in $P6_3/mmc$)
$R=4.6\%$

FIG. 3. The observed magnetic form factor for uranium in UPdSn. The dashed line is the $5f^4$ form factor from Ref. 6, while the solid line is for $F=1.141\langle j_0\rangle+1.845\langle j_2\rangle$. The first six magnetic reflections are indexed, as are those 0l0 reflections that are observed.

were observed for each pair of domains. A slice through the reciprocal space is shown in Fig. 2. The observed magnetic intensities were then corrected for the effects of absorption and extinction in the sample, using the parameters obtained from the fit to the nuclear structure, but accounting for the fact that each magnetic-domain pair has only one-third of the volume of the total crystal. They were then fit to the magnetic structure shown in Fig. 1 in magnetic space group P_c2_1. Detailed arguments as to why this is the correct magnetic space group have been given previously in Ref. 2, and the same reasoning applies to the data reported here. In short, all magnetic reflections can be indexed in the orthorhombic cell shown in Fig. 1, and with the selec-
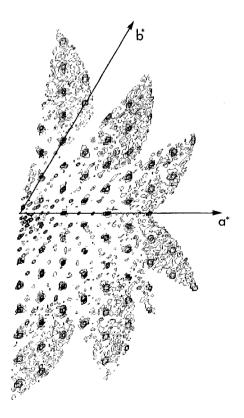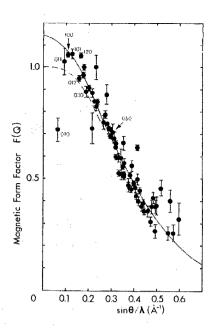

FIG. 2. The $(h,k,0)$ plane through the reciprocal space of UPdSn at 37 K. This figure as a composite of data were taken in seven of the 13 different crystal orientations measured at this temperature. The data have been corrected for the variation of the incident neutron spectrum and the background has been subtracted. The axes represent hexagonal reciprocal lattice vectors.

tion rule that $h+k$ is odd. This necessarily implies that the magnetic cell is c-side anticentered. Second, the presence of reflections with l odd implies that the structure is noncollinear. Of two possible magnetic subgroups, P_Cmc2_1 was preferred on intensity grounds for phase I, but the 010 reflection is absent in this group. Finally, there is only one way to add an x component to the moment and gain intensity in the 0l0 reflections, and that is the P_c2_1 structure shown in Fig. 1. In Fig. 3, we give indices for some of the reflections observed in the present study. Note that they all obey the $h+k=2n+1$ selection rule, that there are some $l=2n+1$ reflections (e.g., 011 and 101) and that the reflections 010, 030, and 050 are present, albeit weakly. Therefore, even though the crystal is nominally in phase I (in which the 0l0 reflections are absent), we have analyzed the data assuming the more general phase II structure. In fitting, the proportions of the sample in each of six possible domains were treated as variables. They occur in three pairs, with the fitting process being rather insensitive to the proportion in each domain within a pair—it is only $h\neq0$, $k\neq0$, $l\neq0$ reflections that have differing structure factors. Assuming the atomic form factor due to Freeman et al.,[6] we obtain the parameters given in Table II. These are in good agreement with previous powder work and the three domain pairs are populated almost equally. Assuming these parameters, we can also plot out the observed uranium magnetic form factor, and this is shown in Fig. 3. For the sake of clarity and so as not to bias the results to the high side, beyond $\sin\theta/\lambda=0.42$, we have only plotted the results if three or more equivalent reflections were observed. Of course the larger error bars occur for the weaker reflections. We observe some deviation from the single-ion form, especially at small momentum transfer. The form factor can in turn be fitted to a sum of orbital and spin

TABLE II. Refined magnetic parameters for UPdSn at 37 K.

Uranium moment	$\mu = 0.863 \pm 0.001 \mu_B$
Canting angles	$\phi = 56.51 \pm 0.15°$
	$\theta = 21.42 \pm 0.34°$

Proportion of crystal in each domain pair:

1	$32.06 \pm 0.22\%$
2	$36.27 \pm 0.21\%$
3	$31.67 \pm 0.23\%$

Reduced $\chi^2 = 2.9$

components,[7] assuming the radial integrals $\langle j_0 \rangle$ and $\langle j_2 \rangle$ given by Brooks, Johansson, and Skriver.[8] This fit is also shown in Fig. 3, with $\mu_L = 1.59 \mu_B$ and $\mu_S = -0.61 \mu_B$. This gives an orbital to spin moment ratio $-\mu_L / \mu_S = 2.62 \pm 0.05$. Following the approach of Lebech and co-workers,[7] this ratio is more characteristic of the trivalent state, rather than the tetravalent. We tentatively conclude that the uranium ion in UPdSn is in the trivalent f^3 state.

ACKNOWLEDGMENTS

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