Temperature dependence of magnetic order in UPdSn

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The intermetallic compound UPdSn has been studied by means of neutron powder diffraction on a two-axis spectrometer. At the lowest temperature, it is a noncollinear antiferromagnet with magnetic space group P_c2_1, and a uranium magnetic moment of $(2.05\pm0.04)\mu_B$, in agreement with previous work. The structure can be described in terms of the magnitude of the uranium magnetic moment μ and two independent canting angles θ and ϕ. ϕ is the angle between the magnetic moment and the c axis; θ is the angle between the in-plane component of the magnetic moment and the b axis. There is no detectable temperature hysteresis in the magnetic order. All three model parameters (μ, θ, and ϕ) vary continuously with temperature, and there is no evidence from our data of any sharp transitions below the Néel point of 43 ± 2 K. The angle ϕ is almost constant over the whole temperature range, while the magnetic moment decreases continuously until it disappears just above 40 K. The angle θ decreases continuously up to a temperature of about 35 K, where it appears to rise again. In the course of this work, we have also demonstrated the consistency of the results for magnetic systems, whether they are measured by the conventional reactor constant-wavelength technique or by the time-of-flight method on a pulsed spallation source.

I. INTRODUCTION

The intermetallic compound UPdSn is one of a set of ternary (1:1:1) uranium-based compounds surveyed using a wide variety of experimental techniques by Palstra *et al.*[1] In general, these materials have quite large resistivities and there is some evidence for the presence of semiconducting gaps. The electronic specific-heat coefficient γ is rather small as compared with those of other uranium intermetallics. The uranium-uranium spacing is greater than the Hill limit, beyond which magnetic ordering is to be expected. In a previous article,[2] we showed that UPdSn crystallises in the hexagonal GaGeLi structure, which is an ordered form of the $CaIn_2$ structure type. On the basis of susceptibility measurements, it was originally thought to order antiferromagnetically at approximately 29 K,[1] but more recent data[2] indicated that there might be two transitions at approximately 40 and 25 K. In fact, there is a shoulder just visible on the high-temperature side in the original susceptibility measurements. Furthermore, recent specific-heat measurements[3] show the presence of two distinct peaks at 26 and 36 K. Our neutron diffraction measurements at the Los Alamos spallation source showed that the low-temperature magnetic structure is as shown in Fig. 1, with a uranium magnetic moment of $2.0\mu_B$. The relative signs of the components of the magnetic moments are listed in Table I. Two canting angles are needed to describe the structure: ϕ is the angle between the magnetic moment and the c axis, while θ is the angle between the in-plane component of the moment and the b axis. These are spherical polar coordinates but with θ and ϕ reversed with respect to the normal convention. In the intermediate phase, between 25 and 40 K, the angle θ was close to or equal to zero. The most definitive signature of the low-temperature structure was the presence of a (010) magnetic Bragg reflection. It seemed that there were two distinct noncollinear magnetic phases—one in which the magnetic moments lie in the orthorhombic b-c plane, and the other (low-temperature) phase in which the magnetic moments had rotated out of that plane. In other words, the sequence of space groups would be

$Cmc2_1$ (the orthorhombic form of $P6_3mc$)
paramagnetic at high temperature ($T>43$ K)

TABLE I. The components of the magnetic moments on the four uranium atoms in UPdSn (see Fig. 1).

Uranium atom position r (in the orthorhombic cell)	Components of the magnetic moment μ
0,0,1/4	μ_x,μ_y,μ_z
0,0,3/4	$\mu_x,\mu_y,-\mu_z$
1/2,1/2,1/4	$-\mu_x,-\mu_y,-\mu_z$
1/2,1/2,3/4	$-\mu_x,-\mu_y,\mu_z$

where $\mu_x=\mu\sin\theta\sin\phi$
$\mu_y=\mu\cos\theta\sin\phi$
$\mu_z=\mu\cos\phi$

to

$$P_c mc2_1 \quad 25 < T < 40 \text{ K}$$

to

$$P_c 112_1 \text{ (or in the more conventional notation } P_c 2_1) \qquad T < 25 \text{ K} .$$

As measurements were only made at three temperatures in the magnetically ordered phases, it was not possible to tell whether the angles changed continuously, or whether there were discrete jumps at the two transitions. Furthermore, the previous measurements were done in heating from 13 K, and there seemed to be a small remnant of the (010) reflection, even in the intermediate phase. If true, this would indicate that the canting angle θ was changing continuously and that there were not two distinct phases. But the remnant intensity could also have been due to temperature hysteresis. In order to clarify these two points, we have undertaken a more careful study of the temperature dependence, with measurements both on heating and cooling, at the Research Reactor of the National Institute of Standards and Technology. We will show that hysteresis is negligible and that the canting angle θ does indeed vary continuously with temperature.

II. EXPERIMENTAL METHOD

The sample was the same one used in the Los Alamos study. It had been prepared as reported previously[1,2] 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 2–3 weeks. 8.0 g of sample were ground and enclosed with helium gs in a sealed vanadium tube. This was, in turn, sealed in a helium atmosphere in an aluminium-alloy tube and mounted in a computer-controlled closed-cycle refrigerator. We used the *BT*-9 triple-axis spectrometer, at the NIST Research Reactor, in two-axis mode with a vertically focusing pyrolytic-graphite monochromator and graphite filter. The wavelength was 2.3505 Å. The analyzer had been removed and the collimation was 40′/30′/40′. For the (010) reflection at 8 Å, this configuration gave a d-spacing resolution $\Delta d/d$ of approximately 9.5%, compared with approximately 2% for the 40° banks on HIPD at Los Alamos. The relatively coarse resolution was chosen to maximize the integrated intensity. As the crystallographic structure and the magnetic structures had already been determined at Los Alamos, and there were three independent magnetic order parameters (the uranium magnetic moment μ, and the canting angles θ and ϕ), it was necessary to measure the intensities of at least three magnetic reflections. In addition we needed one nuclear reflection for normalization purposes. We chose to take more than the minimum amount of data, and measured the four well-separated magnetic reflections (010), (011), (100), and (012). We used the (111),(021) nuclear reflection for normalization, just as in the Los Alamos work. We started out by making complete peak scans, for 1 minute per point at 2 K intervals between 50 and 10 K, on both cooling and heating. Once we had determined that there was no hysteresis and that the peaks neither moved nor broadened, we improved our statistics by measuring the peak intensities for 5 minutes per point at 0.5 K intervals. The measurement is now more susceptible to some types of systematic error, for instance, in subtracting the background and assuming the peak widths to be constant, but the statistical precision is much greater. And other types of possible systematic error, such as those associated with movement of the instrument, can be excluded.

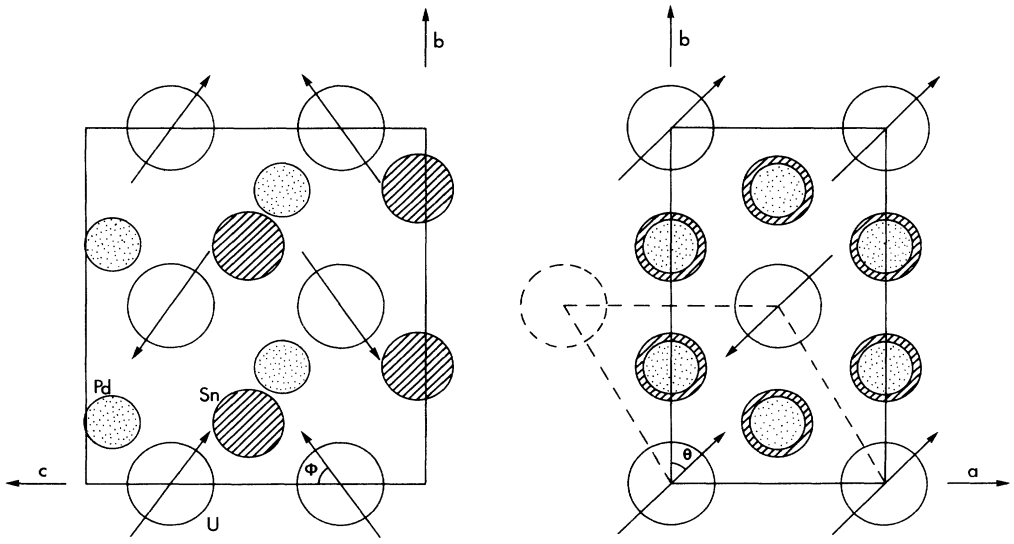

FIG. 1. The magnetic structure of UPdSn, with magnetic space group $P_c 112_1$. The right-hand figure shows the projection onto the orthorhombic a,b plane, which is the same as the hexagonal basal plane. The hexagonal cell is shown by the dashed lines. The left-hand figure shows a projection onto the orthorhombic b,c plane. The angle ϕ is approximately 54° and, at the lowest temperature, the angle θ is approximately 45°. The atoms are plotted with half their respective atomic radii; in order of increasing radius they are Pd, Sn, and U.

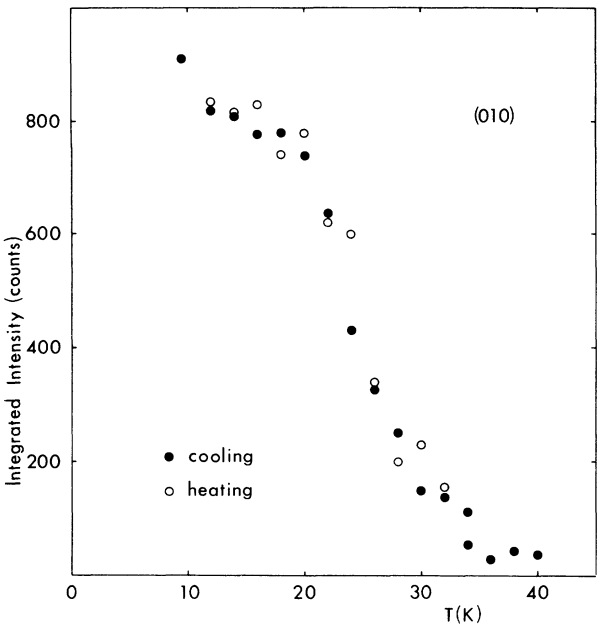

FIG. 2. The variation of integrated intensity in the (010) magnetic reflection. The solid circles represent data taken on cooling, while the open circles represent data taken on heating. Note that there is intensity in the reflection above 25 K, even on cooling, and that there is no significant difference between cooling and heating data.

The peak scans were all fitted to a gaussian lineshape and integrated intensities were then extracted. These were in turn corrected for the variation of the Lorentz factor for cylindrical sample geometry[4] by $\sin\theta \sin(2\theta)$. After further correction for the uranium magnetic form factor,[5] the data were fitted to the noncollinear model described in the Introduction and shown in Fig. 1. This model has three adjustable parameters, μ, θ, and ϕ.

III. RESULTS

The first important result was that there is no significant thermal hysteresis in the measured intensities. This can be seen in the variation in intensity of the (010) magnetic peak shown in Fig. 2. Note that there is significant intensity, on cooling, even above 25 K. It was to explain this intensity, on heating, that we had previously invoked substantial hysteresis as a possible explanation. These data alone are enough to prove the hysteresis idea incorrect. Indeed, the heating and cooling curves lie on top of each other, with no significant difference between them.

As stated in the previous section, the peak scans were fitted to a gaussian lineshape and integrated intensities were extracted for each temperature measured. These were then fitted to the noncollinear magnetic model shown in Fig. 1 and Table I. The variations with temperature of the fitted parameters, μ, ϕ, and θ are shown in

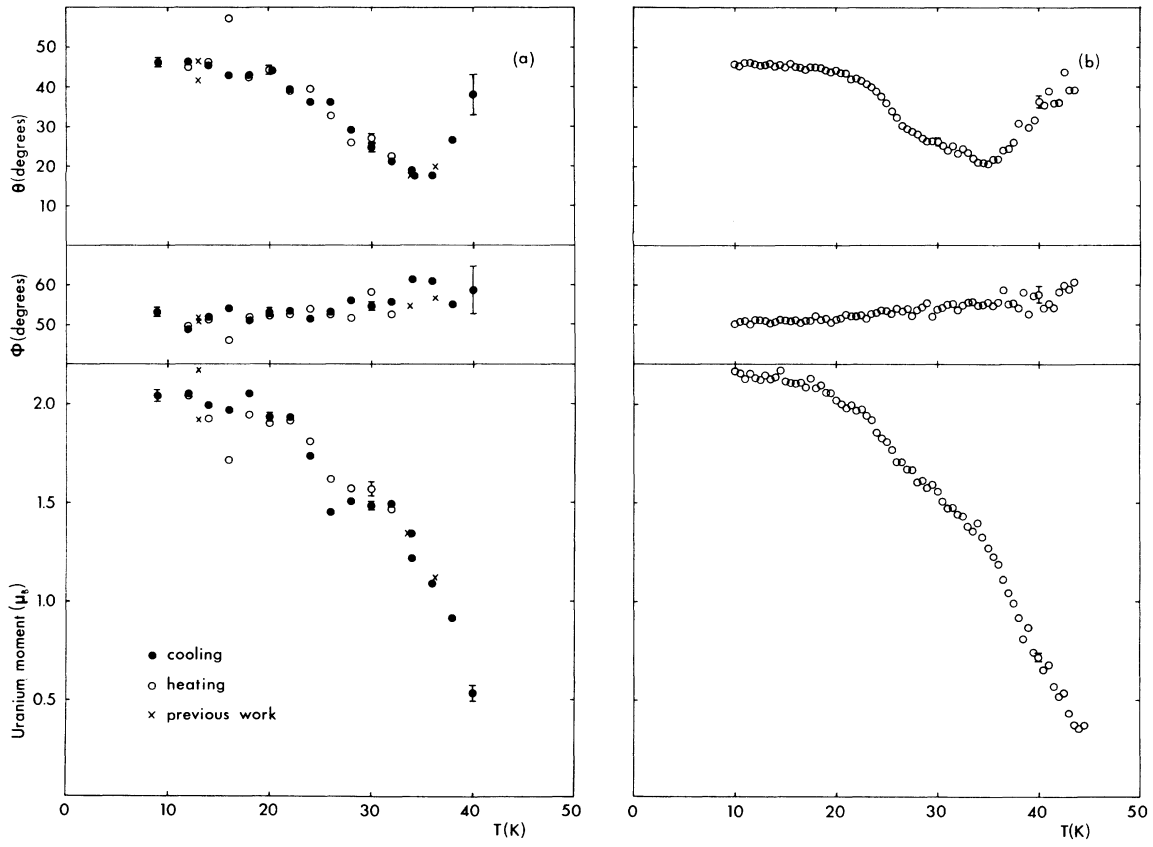

FIG. 3. The variation of model parameters μ, θ, and ϕ, with temperature as extracted (a) from integrated intensities and (b) from peak intensities. The solid circles represent data taken on cooling, while the open circles represent data taken on heating. The crosses represent data taken previously on HIPD at Los Alamos and reported in Ref. 2.

TABLE II. Indexing and Intensities of magnetic reflections in UPdSn at low temperature.

Hexagonal indices	Orthorhombic indices	Observed intensity[a] in the previous work[2] at 13 K	Observed intensity[b] in this study at 14 K
1,2,0,0	010	0.143±0.003	0.153±0.007
1/2,0,1	011	0.147±0.003	0.164±0.009
1/2,1/2,0	100	0.144±0.003	0.131±0.009
1/2,1/2,1	101	0.212±0.004	
1/2,0,2	012	0.397±0.005	0.446±0.025
1,1/2,0	120	0.226±0.006	
1/2,1/2,2	102	0.361±0.008	

[a] $I_{hkl}d_{111}^4/(I_{111}d_{hkl}^4)$.
[b] $I_{hkl}\sin\theta_{hkl}\sin(2\theta_{hkl})/[I_{111}\sin\theta_{111}\sin(2\theta_{111})]$.

Fig. 3(a). Our previous results[2] are also shown as crosses: the agreement is remarkably good. We list the set of integrated intensities obtained using the two different techniques in Table II. Again, through the resolution effects, the Lorentz factors and the scan variables (neutron wavelength for the spallation source and Bragg angle for the reactor) are completely different, there is good agreement for each of the reflections measured. As for the variation of the model parameters, Fig. 3 confirms our previous observation that the canting angle ϕ varies very little with temperature. If anything, there is a slight increase with temperature. On the other hand, θ varies strongly. From saturation at 45° at low temperature, the magnetic moments rotate towards the *b-c* plane. If one ignores the two highest-temperature points, one would say that θ goes to zero at the transition. This would be in agreement with the space group hierarchy described in the Introduction, and the transition could be second order. If one extrapolates both μ and θ to higher temperatures, we derive a Néel temperature of 43±2 K.

A further result is that there was no evidence in the fits that the peaks broadened at all, or that their positions changed in a way other than can be explained by the small effect of thermal expansion. This is important, in that it provides justification for peak-intensity measurement. One simply sets the detector arm at a given peak maximum and varies the sample temperature. By this means, one can achieve much better statistical precision.

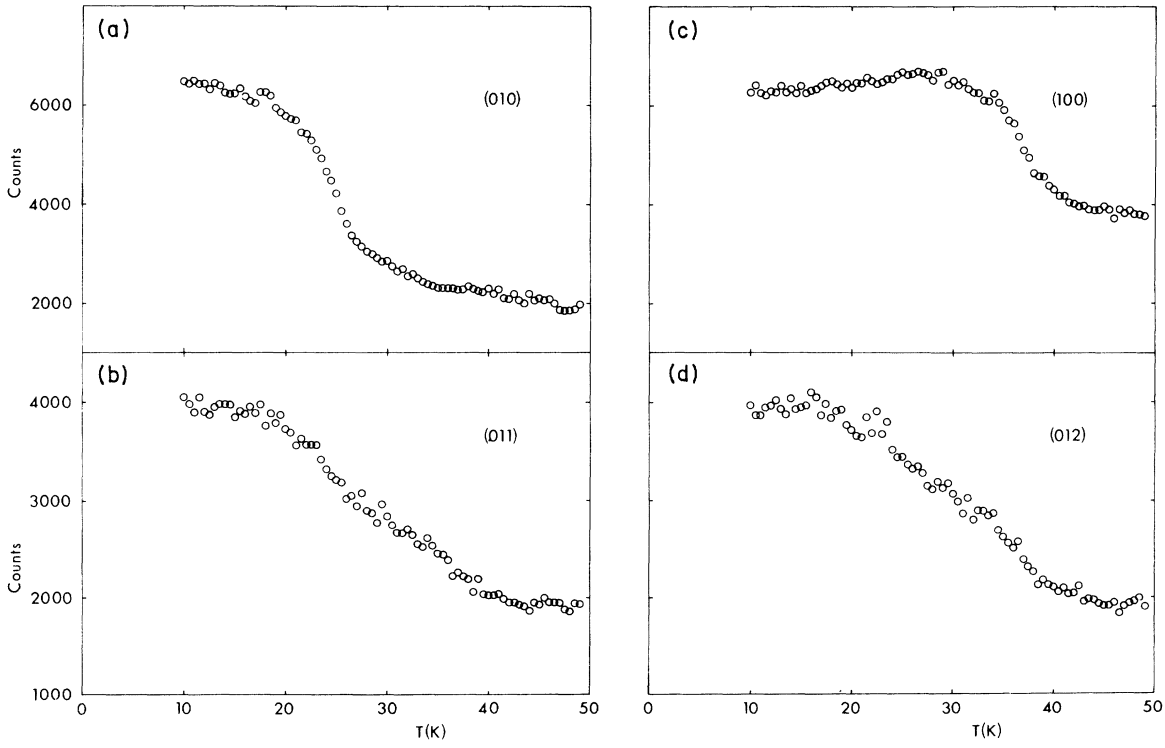

FIG. 4. The variation in peak intensity with temperature for the following magnetic Bragg reflections: (a) (010), (b) (011), (c) (100), and (d) (012). The intensity of the (010) reflection is proportional to μ_x^2, while that of the (100) reflection is proportional to μ_y^2. Note that their behaviors are very different, while the other reflections are intermediate in character. These data were recorded for 5 minutes per point, except for the (100) reflection (10 minutes per point).

These temperature scans are shown in Fig. 4. The behaviors of the peaks are very different, indicating that there is no single simple order parameter. The extremes are the (010) reflection which builds up slowly, starting at 40 K, with a sharp rise between 20 and 25 K, and the orthogonal (100) reflection which gains intensity rapidly below 40 K, reaches a maximum at around 25 K, before dropping slightly beyond that. These two reflections correspond to symmetry axes of the orthorhombic magnetic reciprocal lattice. The other two reflections shown in Figs. 4(b) and 4(d) show intermediate behavior. In fact, within our model for the magnetic structure of UPdSn, the intensities of the (010) and (100) reflections are proportional to the squares of the orthogonal in-plane components of the moment:

$$I_{010} \propto \mu_x^2, \quad I_{100} \propto \mu_y^2 \tag{1}$$

while the (001) reflection is systematically absent.

Figure 3(b), shows the result of fitting the intensities in Fig. 4 to the noncollinear model described in the Introduction. A linear background has been subtracted and the correction has been made for the variation in instrumental resolution, in addition to correction for the Lorentz factor and magnetic form factor. Again the magnetic moment follows a smooth curve with temperature. The canting angle ϕ is almost temperature independent, while the second canting angle θ changes a lot. It is rather ill determined at the Néel point, but rises from a small value to reach saturation at 45° at low temperature. Note that there do not seem to be any major discontinuities in the temperature variations of any of the parameters, except at the Néel point. We remark that while Fig. 3(b) gives a better measure of relative changes in the model parameters, Fig. 3(a) is less susceptible to systematic errors, for the reasons given in the previous section, and the absolute values of the model parameters should therefore be taken from it.

IV. DISCUSSION

We have used spherical polar coordinates, albeit with the labeling of θ and ϕ reversed from the normal convention, as the order parameters describing the magnetic structure(s) and phase transition(s) in UPdSN. As the magnetic cell is orthorhombic, it might make more sense to think in terms of Cartesian components of the magnetic moment μ: (μ_x,μ_y,μ_z). Therefore, in Fig. 5, we show the variation of these Cartesian components with temperature. The x component follows the variation of the (010) peak, following Eq. (1), the y component follows the variation of the (100) peak, and the z component seems to follow the variation of the total moment (see lower panels of Fig. 3). As the angle ϕ is almost constant, this is to be expected. It is interesting to note that the steep rises (as a function of temperature) correlate well with the peaks in the susceptibility.

We believe that the apparent rise in θ close to the Néel temperature is due to the fact that the "background" level of the (010) reflection is not constant above 40 K in Fig. 4(a). There is clearly some extra magnetic scattering present in this "background," possibly originating from

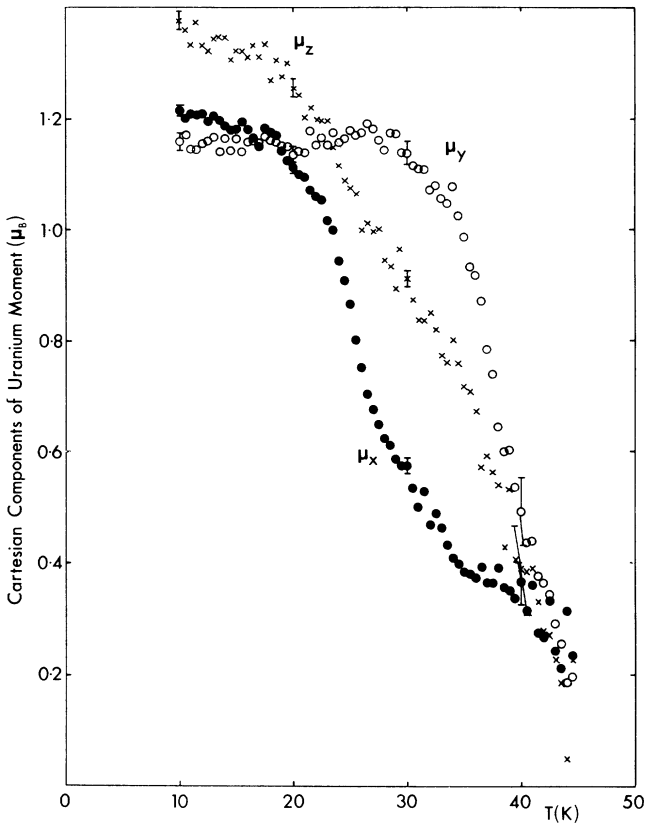

FIG. 5. The variation of the Cartesian components of the moment, μ_x, μ_y, and μ_z (in Bohr magnetons), with temperature, as extracted from the peak intensities shown in Fig. 4.

the powder-averaged critical scattering. Thus, it might be that the upturn in θ is simply due to the erroneous assumption that this is really due to the ordered moment. This is also reflected, in Fig. 5, in the fact that there are apparently significant components left in all the Cartesian components of μ above 40 K, and that because they are of comparable size, θ will apparently rise again. On the other hand, the upturn might be indicative of a real moment rotation, in which case the phase transition does not occur as previously thought. We feel that it is impossible to resolve this question definitively with powder data, and that a single-crystal experiment is necessary. We hope that such single-crystal experiments will be possible in the near future.

Figure 5 can also give one some guidance on the nature of the magnetic anisotropy as might be observed in susceptibility measurements on single crystals. In simple antiferromagnets at low temperature, the transverse susceptibility is much greater than the longitudinal susceptibility,[6] for the simple reason that it costs a lot of exchange energy to reverse the spins and change the longitudinal magnetization, while a transverse magnetization can be achieved, via canting, with a small magnetic cost. For a single-domain single-crystal sample of UPdSn, then, one might expect the c direction (out-of-plane) susceptibility to be the smallest at low temperature and the in-plane (a and b directions) susceptibility to be greater. The picture that emerges from this work seems to be at variance with

the recent specific-heat data of Yuen,[3] in which there are two peaks. Our data indicate that the magnetic moment rotation is continuous and we now have no evidence, from the neutron-scattering results alone, of a second-phase transition. This is something of a puzzle and we hope to resolve it with a single-crystal experiment.

We have shown that there is negligible temperature hysteresis in the magnetic order of UPdSn and that the magnetic moment and canting angles change in a continuous manner: there are no observed discontinuities in any of the order parameters. We have also shown definitively that magnetic diffraction at pulsed spallation sources and steady-state reactor sources yield the same results, even though the instrumental corrections are very different. In fact, this study highlights our previous assertion[7] that spallation sources are well suited to solving completely unknown magnetic structures, while reactor sources are better suited to the observation of the effect of an external variable (temperature, in this case) on a limited number of peaks.

ACKNOWLEDGMENTS

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