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Magnetic site susceptibilities in UPdSn

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Abstract. A study of the magnetization distribution in UPdSn using polarized-neutron scattering is reported. The measurements probed the induced magnetization on a single crystal under an applied magnetic field of 4.6 T \parallel a at 45 K (paramagnetic phase), and the moment aligned with the field at 4 K (ordered state, canted antiferromagnetic phase I). It was found that the distribution of the magnetic moment in the unit cell is rather localized on the actinide atom. The magnetic moment of the U atom aligned by the field is 0.242(2) μ_B at 45 K and 0.431(2) μ_B at 4 K. Any moment on the palladium atom is very small and does not exceed 3% of the aligned moment of the uranium atom at either temperature. The magnetic form factor of the actinide is found to follow closely that of an f^3 electronic configuration, with a small reduction of the orbital moment in the ordered state compared to the free-ion value.

1. Introduction

UPdSn belongs to the large family of ternary UTX compounds of uranium with a transition metal (T) and a p element (X). It was first shown to order antiferromagnetically at low temperatures by Plastra *et al* [1]. A comprehensive study of the bulk properties, including magnetization, susceptibility, Mössbauer, resistivity and specific heat measurements, was reported by de Boer *et al* [2].

Although UPdSn was originally thought to crystallize in the CaIn_2 type of structure with the Pd and Sn atoms disordered and sharing a single crystallographic site, both neutron, x-ray diffraction, and Mössbauer results have shown that it is actually an ordered compound in which Pd and Sn occupy distinct sites [2, 3]. The ordered structure is non-centrosymmetric, the so-called CaGeLi type of structure. It is interesting to notice that the distance between two nearest-neighbour uranium atoms is $c/2 = 3.63 \text{ \AA}$, which is larger than the Hill limit beyond which magnetic ordering is expected for uranium compounds.

Susceptibility measurements show that UPdSn orders antiferromagnetically below 40 K and another magnetic phase transition occurs at 27 K. The magnetic properties are strongly anisotropic with the c -axis as the hard-magnetization direction. Nearly equivalent behaviour was found for fields along the a - and b -axes [2]. The magnetic anisotropy field estimated from high-field measurements is about 110 T. The electronic specific heat coefficient is rather small ($\gamma = 5 \text{ mJ mol}^{-1} \text{ K}^{-2}$) compared to those for other uranium intermetallics.

This compound has been the subject of a number of neutron scattering studies [3–9], on both polycrystalline and single-crystal samples, to determine the magnetic phase diagram.

These studies have shown that below 37 K UPdSn orders in a non-collinear antiferromagnetic structure in which the U moments lie in the bc -plane. At 25 K a transition to another phase is observed, in which the moments are found to deviate from that plane. The magnetic symmetries of the two phases are orthorhombic (phase I) and monoclinic (phase II), described by the magnetic space groups $P_Cm'c2_1$ and P_C112_1 , respectively. Magnetically driven structural phase transitions with orthorhombic and monoclinic symmetries as expected from these space-group assignments have been observed in high-resolution neutron powder diffraction experiments [6]. The latest experiments performed on a single crystal give evidence that μ_y and μ_z order at about 37 K while the component μ_x orders only at 25 K, and exhibits only short-range order above this temperature [5]. The ordered uranium moment at low temperature is $2.05 \mu_B$ which is a relatively large value for a uranium intermetallic. This and the relatively small value of the measured electronic specific heat coefficient were considered to constitute an indication that the behaviour of the 5f electrons in UPdSn was closer to localized than to itinerant. This assumption was however in contradiction with reported results from photoemission studies in which the 5f states were found to lie close to the Fermi energy. The nature of the 5f electron states was discussed by Trygg *et al* [10], who were the first to report a band-structure calculation for this compound. Assuming a collinear ferromagnetic phase and treating the electrons as itinerant in their LDA calculations, good agreement was obtained for the value of the ordered magnetic moment. However, the calculations did not agree with the low value of the electronic specific heat coefficient found by experiment, and the calculated DOS did not reproduce the photoemission spectrum well. Trygg *et al* concluded that describing the 5f electrons as itinerant in UPdSn was probably inadequate.

Recently, another theoretical study of UPdSn was reported by Sandratskii and Kübler [11] who have performed fully relativistic LDA band-structure calculations in the atomic sphere approximation. The Hamiltonian included a scalar relativistic term, spin-orbit coupling and an effective orbital term to account for Hund's second rule. Symmetry arguments show that a non-collinear magnetic structure does not destroy the symmetry of the Kohn-Sham Hamiltonian in UPdSn, and therefore the realization of a minimum of the total energy by a collinear structure is improbable and the moments will deviate from collinearity. The calculated U moment is very close to the experimental value and theory and experiment agree on the directions of the moments in phase II; however, the calculated tilt angle of the moments out of the bc -plane in phase I was smaller than the experimental result. The most remarkable feature of the DOS was a local minimum at E_F which results in a low value of $\gamma = 7.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$. There is a large peak in the DOS at the bottom of the valence band in an energy interval from about -0.35 to -0.15 Ryd of E_F and a group of peaks from -0.15 to 0.15 Ryd. The lower-energy peak is predominantly due to Pd 4d states and the group of peaks at around E_F is mainly due to the U 5f states. Although the two peaks are well separated in energy, there is some hybridization between the U 5f, U 6d, Pd 4d and Sn 5p states.

The theoretical study by Sandratskii and Kübler [11] has shown that an itinerant-electron picture for the 5f electrons is able to predict a density of states which fits the measured photoemission spectrum while reproducing the small value of the electronic specific heat coefficient, γ . The LDA band-structure calculation also gave detailed information about the magnetization distribution in UPdSn. The spin and orbital components of the uranium moment are calculated as $-2.23 \mu_B$ and $4.24 \mu_B$, giving a total moment of $2.01 \mu_B$ per U atom. The ratio $\mu_L/\mu_S = -1.90$ which is significantly below the $5f^3$ free-ion value of -2.56 and indicates a significant reduction in the effective orbital moment. As a result of hybridization between the f electrons and the conduction states of the ligands, it was predicted that small induced moments exist on the Pd and Sn atoms of values $0.04 \mu_B$ and $0.02 \mu_B$, respectively.

It would certainly be of interest to test these detailed theoretical predictions against

experiment and verify how well the LDA describes the magnetization distribution in this compound. This is only possible using a probe of the magnetization distribution which is sensitive to small magnetic moments, as is the case for polarized neutrons. Therefore we have undertaken a polarized-neutron scattering experiment on a single crystal of UPdSn with the aim of accurately mapping its magnetization distribution and analysing the magnetic form factor of the uranium atoms to determine their spin and orbital components.

The possible existence of a sizable magnetic moment on the ligand atoms is in itself an interesting subject. For other ternary uranium intermetallic compounds with a 3d transition metal it has been found that a significant fraction of the magnetization was due to the transition metal atoms. Such was the case for the UTX compounds URhAl [12] and URuAl [13], and to a smaller extent UCoAl [20], which all crystallize in the ZrNiAl type of structure. It was argued that anisotropic hybridization between the 5f and 3d states would actually make a significant contribution to the high uniaxial magnetic anisotropy of these compounds [13]. To what extent similar effects exist if the transition metal is a 4d element also deserves investigation.

2. Experimental details and results

The polarized-neutron scattering measurements were performed at the ILL, France, on the D3 diffractometer. An incident wavelength of 0.843 Å was selected by Bragg reflection from a Heusler monochromator which also acts as a polarizer. An Er filter was inserted after the monochromator to reduce the $\lambda/2$ contamination of the incident beam to less than 0.3%. The neutron polarization direction was switched parallel and antiparallel to the applied field by a Meissner–Majorana cryoflipper with an efficiency close to unity. The sample was mounted in the variable-temperature insert of an asymmetric split-coil superconducting magnet which produces a magnetic field up to a maximum value of 4.6 T parallel to the ω -axis of the diffractometer.

The experiment was performed on the same single crystal as had been used in previous neutron scattering studies of the magnetic structure [7–9]. 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 axis of the cylinder was about 18° away from the [110] axis. The sample was mounted on the diffractometer with the hexagonal a -axis parallel to the ω -axis of the instrument and to the applied magnetic field, so that reflections of the form $(0kl)$ were accessible on the equatorial plane. The D3 diffractometer uses normal-beam geometry which allows measurement of flipping ratios of reflections with $h \neq 0$ by tilting the detector out of the equatorial plane by up to 15°. However, because the a -axis is rather short (4.611 Å), we could only access the $h = 0$ and $h = 1$ layers.

Two data-sets were measured during the experiment. The first set was measured in the paramagnetic phase close to the 40 K transition at a stabilized temperature of 45.5(3) K. This data-set probes the magnetization *induced* by an applied magnetic field of 4.62 T parallel to the hexagonal a -axis. A second data-set was measured in the ordered state (4.6 T, 4.0 K) probing the ferromagnetic component aligned parallel to the field in the non-collinear low-temperature ferrimagnetic phase (canted phase I). A total of 214 reflections were measured in the paramagnetic state, corresponding to a unique set of 68 symmetry-independent reflections. The counting time spent per reflection was about 15 min. In order to improve the counting statistics, the measurement of a small subset of weaker reflections was repeated two or three times. The crystal was then cooled to 4 K under the applied magnetic field of 4.6 T and a second set of 149 reflections (58 unique) was measured in the ordered state. The flipping ratio of the (010) reflection was monitored while cooling. The temperature was lowered in steps of 2 K and sufficient time (900 s) was allowed for sample thermalization before each measurement.

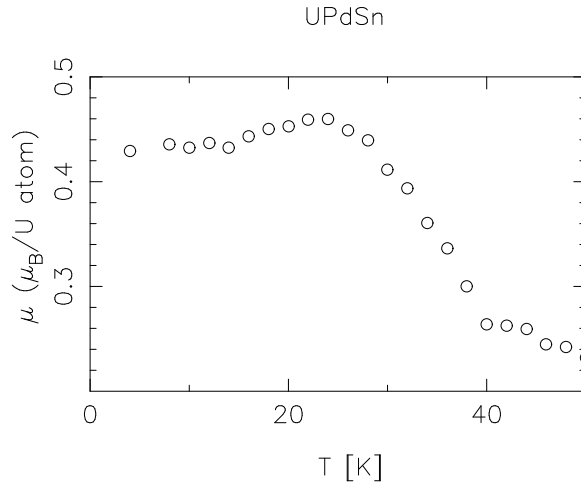


Figure 1. The magnetic moment on the uranium atom as function of temperature determined from the evolution of the flipping ratio of the (010) reflection under a field of 4.6 T \parallel a , monitored while cooling down.

The evolution with temperature of the ordered moment aligned with the applied magnetic field is shown in figure 1. The onset of magnetic ordering takes place at 40 K in good agreement with previous measurements.

3. Data analysis

UPdSn crystallizes in a non-centrosymmetric space group (see table 1) which leads to certain difficulties in the analysis of the polarized-neutron data. In order to show how these difficulties were surmounted, we shall briefly discuss below the method used for data analysis.

Table 1. Crystallographic data for UPdSn. These data were derived from a time-of-flight neutron scattering experiment performed at 55 K on the same single crystal as was used for this work [9].

Atom	Site	x	y	z
U	2a	0	0	$z = 1/4$ (fixed to define the origin)
Pd	2b	1/3	2/3	$z = 0.4225(12)$
Sn	2b	2/3	1/3	$z = 0.5181(15)$
Space group $P6_3mc$, $a = 4.611(6)$ Å, $c = 7.261(50)$ Å				

Polarized-neutron scattering relies on an interference between the nuclear and magnetic cross-sections for the scattering of a polarized beam of neutrons by a magnetically ordered crystal. The interference only exists if nuclear and magnetic scattering occur at the same place in reciprocal space, a condition that is met for ferromagnets and also for antiferromagnets which have identical crystallographic and magnetic unit cells, like MnF_2 ($\kappa = 0$). UPdSn has an ordering wave-vector $\kappa = (1/2, 0, 0)$ (in the hexagonal lattice) and, according to the magnetic phase diagram reported by Nakotte *et al* [7], at 4.0 K and 4.6 T \parallel a the magnetic structure is canted antiferromagnetic which is related to the zero-field magnetic phase I by adding a ferromagnetic component parallel to the field. In fact, according to the phase diagram the low-

temperature antiferromagnetic phase II is unstable for fields higher than 3.5 T, above which a transition to the canted phase I occurs. Thus, the low-temperature polarized-neutron data will provide a measure of the component of the canted magnetization aligned along the field direction. At 50 K the sample is paramagnetic and we can assume that all magnetization is aligned parallel to the applied magnetic field.

The cross-section for scattering for a Bragg reflection at the reciprocal-lattice vector $\hat{\mathbf{k}}$ of a beam of neutrons with polarization \mathbf{P} is given by

$$\frac{\partial\sigma}{\partial\Omega} = C(N^2(\mathbf{k}) + 2\Re(\mathbf{P} \cdot \mathbf{Q}(\mathbf{k})N^*(\mathbf{k})) + |\mathbf{Q}(\mathbf{k})|^2). \quad (1)$$

In this equation, $N(\mathbf{k})$ is the nuclear structure factor

$$N(\mathbf{k}) = \sum_{j=1}^n b_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) \exp(-B_j|\mathbf{k}|^2/16\pi^2) \quad (2)$$

where the sum extends over the n atoms in the unit cell with positions \mathbf{r}_j , nuclear scattering lengths b_j and isotropic temperature factors B_j , respectively. The magnetic interaction vector, $\mathbf{Q}(\mathbf{k})$, is given by

$$\mathbf{Q}(\mathbf{k}) = 0.2695 \sum_{j=1}^m (\hat{\mathbf{k}} \times \boldsymbol{\mu}_j \times \hat{\mathbf{k}}) f_j(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_j) \exp(-B_j|\mathbf{k}|^2/16\pi^2) \quad (3)$$

where the sum extends over the m magnetic atoms, with moments $\boldsymbol{\mu}_j$ and form factors $f_j(\mathbf{k})$. The numerical factor 0.2695 is the scattering length (in units of 10^{-12} cm) associated with $1 \mu_B$. If all moments contributing to a reflection are collinear, then the vector part of the interaction vector can be taken outside the summation and one can define a magnetic structure factor $M(\mathbf{k})$ such that

$$\mathbf{Q}(\mathbf{k}) = qM(\mathbf{k}) \quad \text{with } q = \hat{\mathbf{k}} \times \hat{\boldsymbol{\mu}} \times \hat{\mathbf{k}} \quad (4)$$

in which $\hat{\mathbf{k}}$ and $\hat{\boldsymbol{\mu}}$ are unit vectors in the directions of the scattering vector and magnetization, respectively. A polarized-beam experiment consists in measuring the *flipping ratios* R , which are the ratios between the intensities of the Bragg reflections measured with the spin parallel (I^+) and antiparallel (I^-) to the applied field. From (1), and defining $q'^2 = \mathbf{P} \cdot \mathbf{q}$, $N = N' + iN''$ and $M = M' + iM''$, the flipping ratios are given by

$$R = \frac{N'^2 + N''^2 + 2q'^2(N'M' + N''M'') + q^2(M'^2 + M''^2)}{N'^2 + N''^2 - 2q'^2(N'M' + N''M'') + q^2(M'^2 + M''^2)}. \quad (5)$$

If α is the angle between the magnetization and the scattering vector \mathbf{Q} and β the angle between the polarization vector and \mathbf{q} , then it is easy to show from (4) that $q^2 = \sin^2 \alpha$ and $q'^2 = p \sin \alpha \cos \beta$. When the polarization and magnetization directions coincide, as is usually the case except when dealing with very anisotropic magnetic systems for which the magnetization is not perfectly aligned with the applied field, $\cos \beta = \sin \alpha$.

For a centrosymmetric structure, the Fourier components of the magnetization and nuclear densities are real numbers and therefore $M = M'$, $N = N'$ and the previous equation can be solved exactly for the single unknown $M = M'$, provided that the nuclear structure factors are known. Defining $\gamma = M/N$, $\epsilon = \cos \beta / \sin \alpha$ and $v = (1 + R)/(1 - R)$,

$$\gamma = -p\epsilon v \pm \sqrt{(p\epsilon v)^2 - \left(\frac{1}{q^2}\right)}. \quad (6)$$

Choosing between the two solutions is generally straightforward, particularly in the case of small magnetic moments for which $|\gamma| \ll 1$. However, If the structure is non-centrosymmetric,

it is not possible to extract from (5) *both* real and imaginary parts of the magnetic structure factors. This does not mean, however, that the polarized-beam method is useless for non-centrosymmetric structures. One possibility is to compare the measured R -values with those calculated for a trial model of the magnetization distribution. If a good enough model is known to start with, it can be refined against the measured data by a least-squares method. A number of polarized-neutron studies, mostly on organic or organometallic compounds, have tackled the problem in this way.

The case of UPdSn is fortunate because it is possible to extract *approximate* values of the magnetic structure factors directly from the measured flipping ratios. This is possible because the main contributors to the magnetization, the uranium atoms, occupy a centrosymmetric sublattice, although the whole structure is not centrosymmetric. In fact, it is only the ordering of the Pd and Sn atoms on two distinct sites which distinguishes the CaGeLi structure from the parent, centrosymmetric, CaIn₂ one. The U atoms are located at the 2a crystallographic sites in the unit cell at positions (0, 0, 1/4) and (0, 0, 3/4). The two uranium layers are separated by $c/2$ and thus do not contribute to Bragg reflections with l odd. Those with l even have a geometric structure factor for the uranium atoms that is either 2 ($l = 4n$) or -2 ($l = 4n + 2$). Thus, if only the uranium atoms carried a magnetic moment, the flipping ratios of those reflections with l odd would ‘sense’ no magnetism at all and their flipping ratios should be unity, and in this case the magnetic structure factors of the l -even reflections are, in fact, real numbers. Indeed, we have observed that the flipping ratios of the l -odd reflections do not differ from unity by more than twice their standard deviation due to the counting statistics. If we make the hypothesis that the moments on the uranium atoms are much larger than those on the palladium and tin atoms, then the approximation $M'' \ll M'$ will hold and terms in M'' can be neglected. Equation (5) can then be solved for the unknown M' . Defining $\gamma' = M'/N'$ and $\tan \phi = N''/N'$,

$$R \sim \frac{1 + \tan^2 \phi + q^2 \gamma'^2 + 2q'^2 + 2q'^2 \gamma'}{1 + \tan^2 \phi + q^2 \gamma'^2 + 2q'^2 - 2q'^2 \gamma'} \quad (7)$$

and

$$\gamma' \sim -p\epsilon v \pm \sqrt{(p\epsilon v)^2 - \left(\frac{1 + \tan^2 \phi}{q^2}\right)}. \quad (8)$$

We have used (8) to derive two sets of magnetic structure factors (45 and 4 K) from the measured flipping ratios, with the approximation mentioned above. We shall show below that this approximation is a very good one in our case.

To break down the magnetic response of UPdSn into individual site susceptibilities, we have fitted the observed structure factors to a model in which the magnetization is built from a superposition of spherically symmetric atomic contributions, located at the sites occupied by the actinide and transition metal atoms, using equation (3). The uranium magnetic form factor was calculated in the dipole approximation [14]:

$$\mu_f(Q) = \mu(\langle j_0 \rangle + C_2 \langle j_2 \rangle) \quad C_2 = \frac{\mu_L}{\mu} \quad (9)$$

where the C_2 -coefficient is the ratio between the orbital (μ_L) and total (μ) moments of the actinide atom. It is useful to relate C_2 to the ratio

$$-\frac{\mu_L}{\mu_S} = \frac{C_2}{C_2 - 1}. \quad (10)$$

Note that the orbital and spin components are opposite, as imposed by Hund’s rules, for these light actinides. In uranium compounds the orbital component is particularly sensitive to the

degree of hybridization between the 5f electrons and the conduction states. Following the application of density functional theory to this problem [15], we may interpret the reduction of the $-\mu_L/\mu_S$ ratio below that of the free ion as a measure of the degree of hybridization between the actinide and ligand wave-functions. Plotting this ratio versus the f-electron count for a number of actinide compounds for which this ratio has been accurately measured by polarized-neutron scattering supports this picture [16].

The $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions used in the least-squares fits were derived from the radial wave-functions calculated by Desclaux and Freeman [17] for a U^{3+} ion using a fully relativistic code. For the palladium atoms, we used a spin-only form factor calculated from the atomic wave-functions of Clementi and Roetti [18]. The amount of orbital moment carried by the 4d atoms is probably quite small; in elemental palladium, it does not exceed 10% of the spin-moment value [19].

Table 2. Magnetic moments on UPdSn derived from a least-squares fit of the magnetic structure factors (I) and flipping ratios (II).

	4 K		45 K	
	I	II	I	II
μ_U (μ_B)	0.426(6)	0.431(2)	0.244(2)	0.242(3)
μ_{Pd} (μ_B)	0.02(2)	0.009(3)	0.002(4)	0.006(1)
C_2	2.00(4)	1.95(4)	1.72(2)	1.73(2)
$-\mu_L/\mu_S$	1.99(6)	2.05(7)	2.39(7)	2.36(9)
wR	4.4%	2.1%	4.3%	1.2%

The results of the least-squares refinement are shown in table 2 (I). A good fit is obtained at both temperatures with the magnetization almost exclusively located at the actinide atoms. The estimated value of the magnetic moment at the palladium atoms is very small.

The magnetic scattering amplitude associated with a single uranium atom is shown as a function of $\sin(\theta)/\lambda$ on a form factor curve for each of two temperatures in figures 2 and 3. To draw these figures we have assumed that *all* of the moment is at the U sites. The fact that all points lie on a reasonably smooth curve further confirms that the induced moments on Pd and Sn are small. The U^{3+} magnetic form factor is also shown on these plots, and it can be seen that the experimental values follow this function closely. The extrapolated values of the magnetic scattering amplitudes for $\theta = 0$ give the value of the magnetic moment aligned by the magnetic field. The values are in very good agreement with magnetization results reported by Nakotte *et al* [8].

A reconstruction of the magnetization distribution in UPdSn, projected along the a -axis, was made using the maximum-entropy method which minimizes the effect of the series termination and provides the least noisy magnetization map compatible with the measured data within the error bars [20]. The calculation was performed with the maximum-entropy code of Sakata *et al* [21, 22] in a version adapted to run under the LINUX operating system by Burger and Prandl [23]. The projection of the magnetization distribution on the bc -plane is shown in figure 4; clearly it is very flat except at the positions occupied by the uranium atoms.

A second refinement of the model was performed *directly* against the flipping ratios using the program MAGLSQ of the CSSL library [24], avoiding in this way the intermediate step of deriving the magnetic structure factors and its inherent approximation. This makes it necessary to use a *non-linear* least-squares procedure, instead of a simpler linear one in the case of fitting to the magnetic structure factors. This is not a major problem if a good starting point for the model is already known and indeed good convergence was obtained after a few least-squares

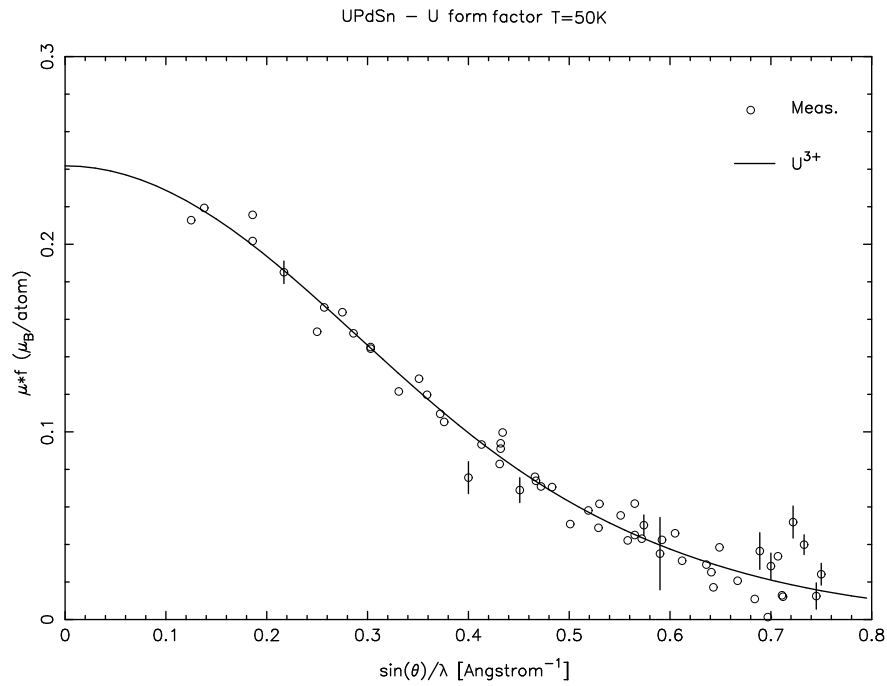


Figure 2. The magnetic scattering amplitude of an uranium atom derived from the set of magnetic structure factors measured at 50 K represented on a form factor plot.

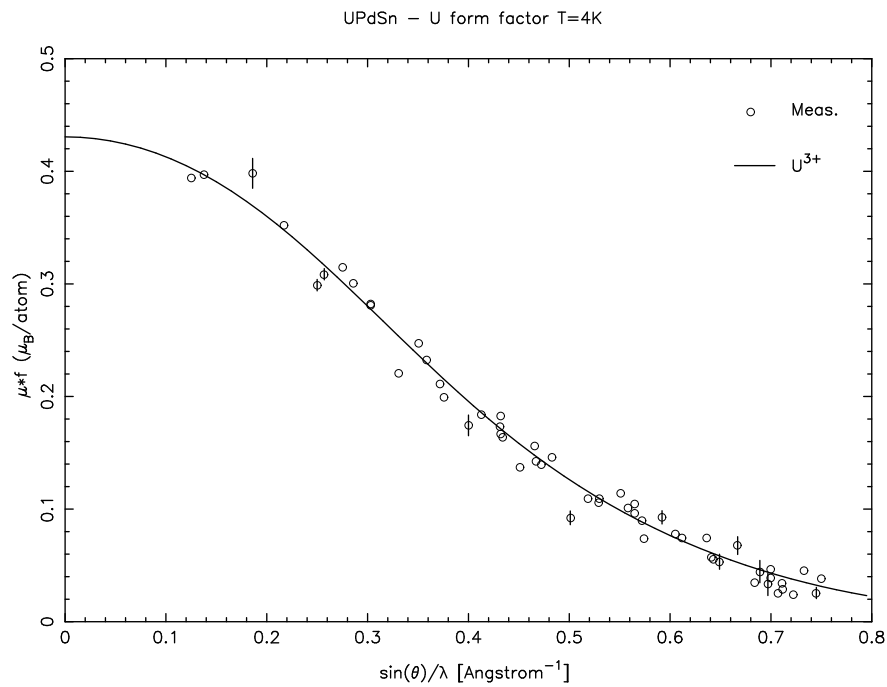


Figure 3. The magnetic scattering amplitude of an uranium atom derived from the set of magnetic structure factors measured at 4 K represented on a form factor plot.

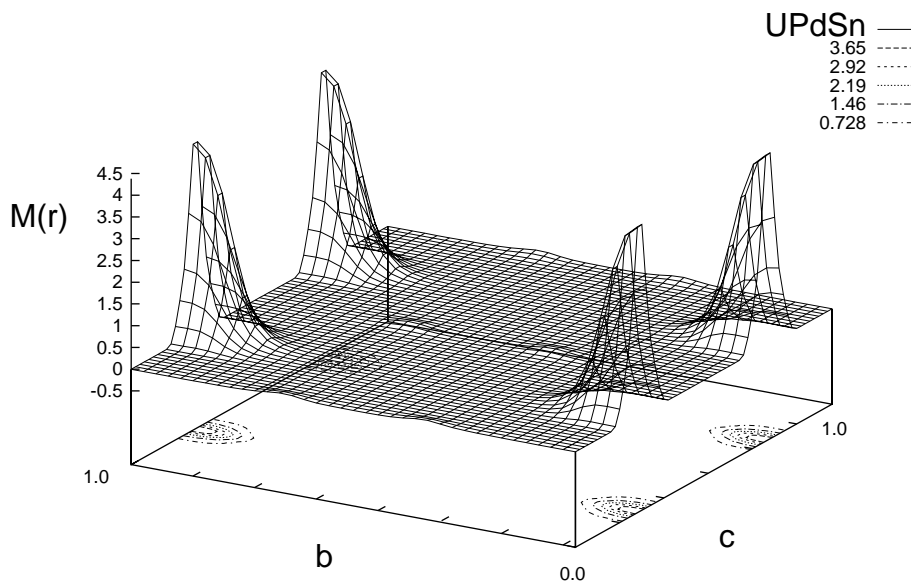


Figure 4. The maximum-entropy map of the magnetization projected on the bc -plane. The contour levels are given in units of $\mu_B \text{ \AA}^{-2}$.

cycles; the results are shown in table 2 (II). We can see that excellent agreement is obtained with the results of the previous refinement against the magnetic structure factors (table 2, I), which shows that the set of structure factors derived under the approximation $M' \ll M''$ is accurate enough to validate the maximum-entropy reconstruction.

4. Discussion

An interesting aspect of the study of the hybridization between 5f electrons and transition metal d states is that it allows one to develop systematics that will be able to guide theoretical efforts. One signature of this hybridization is the appearance of a magnetic moment, or a large magnetic susceptibility in a paramagnetic material, on atoms that normally have a small susceptibility in their elemental form. For example, in previous work [12, 13] we have shown that Rh and Ru d states are readily polarized. On the other hand, it is commonly accepted that UPd₃ is a localized system [25] with a 5f² ground state, not simply because of the observation of crystal-field levels in neutron inelastic scattering but also because of photoemission results, which show the 5f peak below E_F . Theory has satisfactorily explained this localized state in UPd₃. Under these conditions, no magnetic moment would be expected at the Pd site in UPd₃, although this polarized-beam experiment has not actually been performed. A polarized-neutron study of the induced moment in UPd₂Al₃ [26] showed that the ratio of that for the induced palladium to that on the uranium site is $\mu_{\text{Pd}}/\mu_{\text{U}} < 3\%$. The present study shows that for UPdSn also this ratio is less than 3%. Of course, not all of these systems are isostructural, and this will introduce important differences; but we note that the studies of URhAl and URuAl gave $\mu_{\text{T}}/\mu_{\text{U}} \sim 30\%$, where T = Rh or Ru, so there is clearly a *qualitative* difference between Pd and those elements with fewer 4d electrons in the band. One can understand this by realizing that by filling the 4d band on Pd the overall energy may be lowered, at the expense of there

being one less electron in the conduction band.

Sandratskii and Kübler [11] have also addressed theoretically the question of the induced moment on the Pd and Sn sites, but in the ordered state. As explained earlier, the polarized-beam method is insensitive to the major antiferromagnetic component, and senses only the induced component at $\kappa = 0$. The value given by Sandratskii and Kübler is $0.04 \mu_B$ at the Pd site and half of this at the Sn site. Compared to the total moment of $\sim 2 \mu_B$ this represents $\mu_{\text{Pd}}/\mu_U \sim 2\%$, and is clearly close to our upper limit for any induced moment on the Pd site. Our results are thus consistent with the predictions. Such reasoning, of course, assumes that the site susceptibility of the Pd is proportional to the molecular field present as a result of the large susceptibility at the uranium site, but since this susceptibility is itself small, this seems a reasonable assumption.

Unlike UPd_3 , which has been identified as a localized $5f^2$ system, our determination of the value of $|\mu_L/\mu_S|$ as between 2.1 and 2.4 gives strong evidence that the uranium is trivalent, i.e. a $5f^3$ ground state. The free-ion values of $|\mu_L/\mu_S|$ for $5f^2$ and $5f^3$ are 3.29 and 2.56, respectively. Interestingly, the measured $|\mu_L/\mu_S|$ ratio is lower in the ordered state than in the paramagnetic state. The difference is small but appears to be statistically significant and would be consistent with a stronger hybridization, with its associated reduction of the orbital moment, in the ordered state. The measured value of $|\mu_L/\mu_S|$ in the ordered state is also in good agreement with that given by the calculations of Sandratskii and Kübler [11], $|\mu_L/\mu_S| = 1.90$. A value of $|\mu_L/\mu_S| = 2.62(5)$ for this compound was also reported by Johnson *et al* [9] who fit a uranium form factor to the integrated magnetic intensities at 37 K (antiferromagnetic phase I in zero field) measured on a neutron Laue camera. An analysis of magnetic form factors using these data is much less accurate than using polarized-neutron scattering and their optimistic error bar most probably reflects precision rather than accuracy. Although they also concluded that a trivalent $5f^3$ state was the most probable for the uranium atom, the fit was performed using radial functions of an f^2 state which probably explains the higher magnitude of their value of $|\mu_L/\mu_S|$ compared to ours. Unfortunately, Sandratskii and Kübler do not give the $5f$ -electron count from their band-structure calculation. Our measurements are consistent with a localized $5f^3$ state. Given the relatively low symmetry of UPdSn , we have not tested the form factor against possible ground-state crystal-field functions, of which there are many. One aspect that is well known for the $5f^3$ state is that the crystal-field states are usually anisotropic in real space, which leads to a form factor that is far from smooth. This does not seem to be the case in figures 2 and 3, although one would have to perform detailed calculations to verify this. It appears more likely, in our opinion, that the form factor shows a ‘smooth’ behaviour as a consequence of hybridization effects between the U $5f$ and conduction electron states. Such form factors do not yet exist with which to compare experiment and theory, although the most famous experimental one is clearly that of US, measured 25 years ago [27] and found to be remarkably smooth. A better way to proceed would be to perform neutron inelastic experiments and see whether there is evidence for crystal-field states, which are a sure sign of localized $5f$ levels, as are found in UPd_3 but not in US [25]. Such experiments are under way [28] and, together with the present experiments, which suggest a $5f^3$ ground-state manifold, may lead to a deeper understanding of this material.

5. Conclusions

We have undertaken a detailed study of the magnetization distribution in UPdSn using polarized-neutron scattering data. The experiment was performed on a well characterized sample, the same single crystal as was used in previous studies of the magnetic phase diagram.

The magnetization distribution was probed at two temperatures: 45 K (the paramagnetic phase) and 4 K (the ordered state, the canted antiferromagnetic phase I), under an applied magnetic field of 4.6 T parallel to the a -axis. The main result of this study is that the distribution of the magnetic moment in the unit cell is rather localized on the actinide atom. The magnetic moment of the U atom aligned by the field is $0.242(2) \mu_B$ at 45 K and $0.431(2) \mu_B$ at 4 K. Any moment on the palladium atom is very small and does not exceed 3% of the aligned moment of the uranium atom at either temperature. The magnetic form factor of the actinide follows closely that of a trivalent, f^3 electronic configuration. The measured value of the ratio between the orbital and spin moment of the uranium atom in the paramagnetic state is close to the free-ion value, but a smaller value was found in the ordered state, probably due to a reduction of the orbital moment resulting from an increased hybridization between the f electrons and conduction states. The measured value of $|\mu_L/\mu_S|$ at 4 K is in good agreement with the LDA calculations of Sandratskii and Kübler [11].

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