Investigation of magnetic ordering in UPdAs$_2$ by neutron diffraction

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Abstract. Magnetic properties of UPdAs$_2$ were studied by both bulk magnetic measurements and by neutron diffraction. The temperature dependence of the reciprocal magnetic susceptibility $1/\chi$ shows that UPdAs$_2$ orders antiferromagnetically below 240 K. Above 260 K, $1/\chi$ exhibits an almost straight-line behaviour with $\mu_{\text{eff}} = 2.88\,\mu_{\text{B}}$ and $\theta_{\text{p}} = 51$ K. Neutron diffraction experiments confirm the tetragonal space group P4/$n$mm and yielded refined structural parameters. The magnetic ordering in UPdAs$_2$ is of AF IA type with magnetic moments aligned along the c direction. The magnetic structure consists of a stacking of ferromagnetic (001) sheets with a $+ + - -$ sequence along the four-fold axis. The ordered magnetic moment of uranium at 8.7 K amounts to 1.69(5) μ_{B}. The temperature variation of the magnetic (101) peak yields the Néel temperature $T_{\text{N}} = 235$ K.

1. Introduction

Recent experiments (Fischer *et al* 1989) performed on ternary uranium compounds UNi$_2$P$_2$ and UNiAs$_2$ revealed that both systems order antiferromagnetically with Néel temperatures of 101 and 195 K respectively.

Their magnetic ordering corresponds to the configuration of AF I type, i.e. the magnetic moments are coupled ferromagnetically within (001) sheets, but adjacent sheets are arranged antiferromagnetically, yielding the sequence $+ - + - \ldots$ in the c direction. The magnetic moments of uranium atoms are aligned along the c axis.

As a continuation of our earlier studies we present here the results of neutron diffraction studies performed on the compound UPdAs$_2$ which is isostructural with UNiAs$_2$ (Stepień-Damm *et al* 1987). According to preliminary bulk magnetic measurements it orders antiferromagnetically at about 240 K.

2. Experimental details

The polycrystalline specimen of UPdAs$_2$ was obtained from synthesis of the stoichiometric mixture of powdered palladium metal with UAs$_2$ sealed in an evacuated quartz ampoule and annealed at 700 °C for two weeks.

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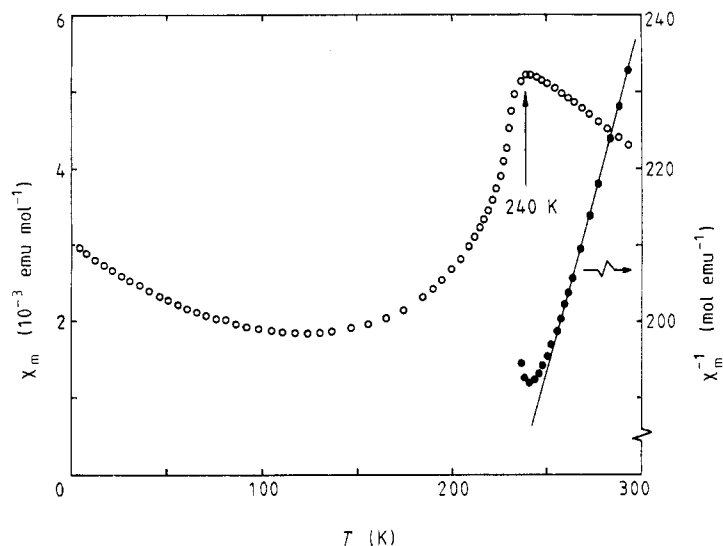
Figure 1. Low-temperature behaviour of the magnetic susceptibility of $UPdAs_2$. The characteristic maximum at 240 K indicates the transition to an ordered antiferromagnetic state.

The x-ray powder diffraction analysis was performed on a DRON 1.5 diffractometer, using Cu Kα radiation. The diffraction pattern obtained could be easily indexed on the basis of the tetragonal lattice parameters $a = 3.99$ Å and $c = 9.49$ Å.

Magnetic susceptibility measurements were carried out by a Faraday method within the temperature range 4.2–300 K, using an RH Cahn electro-balance. For the neutron diffraction investigations the powder sample of $UPdAs_2$ was enclosed under helium gas atmosphere in a cylindrical vanadium container of diameter 8 mm and height 5 cm.

Neutron diffraction measurements were performed on the multidetector powder diffractometer DMC and on a two-axis diffractometer installed at the Saphir reactor in Würenlingen. For the analysis of crystal and magnetic structures, neutron diffraction patterns were recorded with neutrons of wavelength $\lambda = 1.707$ Å, using a closed-cycle helium refrigerator. The dependence of magnetic peak intensity on temperature was measured on the two-axis diffractometer with a neutron wavelength $\lambda = 2.34$ Å. The Rietveld (1969) profile method was used to analyse the neutron diagrams, assuming scattering lengths $b_U = 8.42$, $b_{Pd} = 5.91$, $b_{As} = 6.58$ fm (Sears 1984). The magnetic form factor of uranium was taken in a dipole approximation (Freeman *et al* 1976).

3. Results

The results of the magnetic susceptibility measurements are presented in figure 1. Apparently, $UPdAs_2$ orders antiferromagnetically below the Néel temperature $T_N = 240$ K. Above 260 K the reciprocal susceptibility plotted against temperature shows an almost straight-line behaviour with $\mu_{eff} = 2.88$ μ_B per U atom and $\theta_p = 51$ K. A striking feature seen in figure 1 is a strong upturn in the $\chi(T)$ curve below 110 K. Such behaviour cannot be caused by ferromagnetic impurities, as the magnetic susceptibility at 4.2 K is independent of the applied magnetic field. However, we cannot exclude the possibility

Table 1. Cell dimensions, fractional coordinates, and isotropic thermal parameters for UPdAs$_2$ at 298 and 8.7 K. μ = ordered magnetic moment. R_n and R_m denote the reliability factors for the integrated nuclear and magnetic reflections, respectively. The estimated error of the last digit is added in parentheses. (*a*) 298 K. Cell dimensions: a = 3.987(1) Å, c = 9.493(3) Å, R_n = 5.8%. (*b*) 8.7 K. Cell dimensions: a = 3.973(1) Å, c = 9.480(3) Å, R_n = 6.0%, R_m = 26.1%.

Atom	Position	x	y	z	B (Å^2)	μ (units of μ_B)
(*a*)						
U	2*c*	0.25	0.25	0.2370(2)	0.17(5)	—
As I	2*c*	0.25	0.25	0.6826(3)	0.29(8)	—
As II	2*a*	0.25	0.75	0	0.30(8)	—
Pd	2*b*	0.25	0.75	0.5	0.47(5)	—
(*b*)						
U	2*c*	0.25	0.25	0.2375(2)	0.00(5)	1.69(5)
As I	2*c*	0.25	0.25	0.6827(3)	0.14(6)	—
As II	2*a*	0.25	0.75	0	0.14(6)	—
Pd	2*b*	0.25	0.75	0.5	0.00(5)	—

Table 2. Shortest interatomic distances for UPdAs$_2$.

Atoms	Distance (Å)	Atoms	Distance (Å)
U–4U	3.987(1)	Pd–4As I	2.6417(18)
U–4Pd	3.1949(17)	Pd–1As II	4.7465(15)
U–4As I	2.9207(10)	As I–4As I	3.987(1)
U–1As I	4.2300(35)	As I–4As I	4.4683(41)
U–4As II	3.0060(16)	As I–4As II	3.6129(23)
Pd–4Pd	2.8192(5)	As II–4As II	2.8192(5)
Pd–4Pd	3.987(1)		

that it could be due to the presence of a small amount of paramagnetic impurities. The neutron diffraction data at room temperature confirm the space group P4/$n$mm for UPdAs$_2$ with two U and two As atoms at sites 2c, = $\pm(\frac{1}{4}, \frac{1}{4}, z)$, two As atoms at 2$a$, = $\pm(\frac{1}{4}, \frac{3}{4}, 0)$ and two Pd atoms at 2b, = $\pm(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$. The structural analysis was based on 80 inequivalent hkl values contributing to the powder diffraction pattern. At room temperature the profile refinement gave the unit-cell constants a = 3.987(1) Å, c = 9.493(3) Å. To check for possible deviations from full site occupancies we have, in the final stage of refinement, also varied the occupancy parameters, but no statistically significant deviation from full occupancy was obtained. The final atomic coordinates, thermal parameters and interatomic distances are presented in tables 1 and 2 respectively.

Surprisingly, the neutron diffraction pattern of UPdAs$_2$ taken at 8.7 K was different from that observed previously for the UNiAs$_2$ and UNi$_2$P$_2$ compounds. New magnetic reflections appearing at 8.7 K (compare figure 2) could no longer be indexed on the basis of a single unit cell. The observed reflections followed the rule: $l = (2n + 1)/2$, where $n = 1, 2, 3, \ldots$. This leads unambiguously to the conclusion that the new magnetic unit
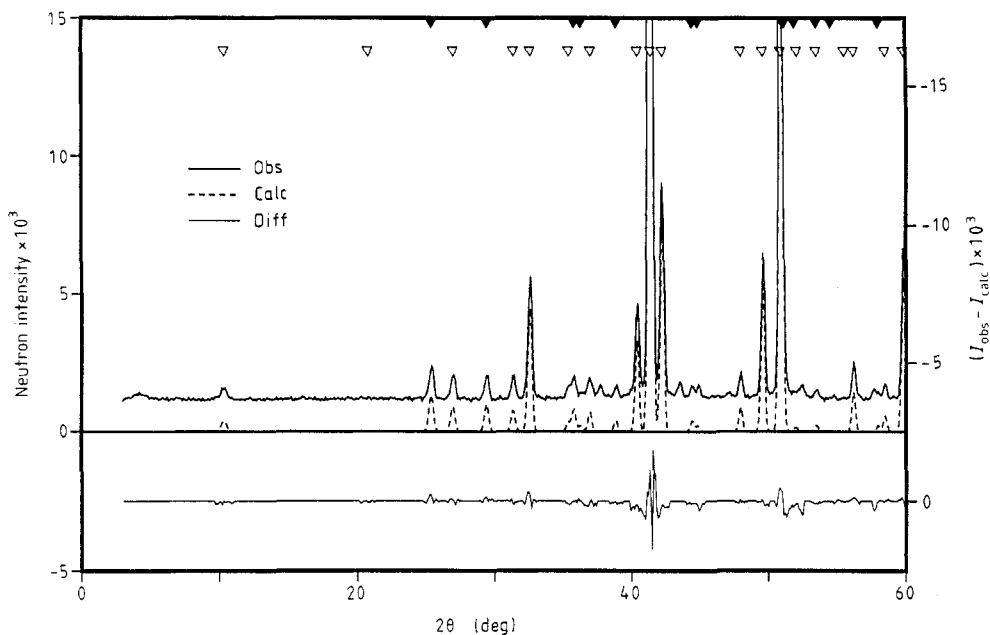
Figure 2. The low-angle part of the neutron pattern of $UPdAs_2$ at 8.7 K, 1.707 Å. Full and broken curves represent the observed and calculated profiles respectively. Triangles (open and full) indicate the positions of nuclear and magnetic peaks respectively.
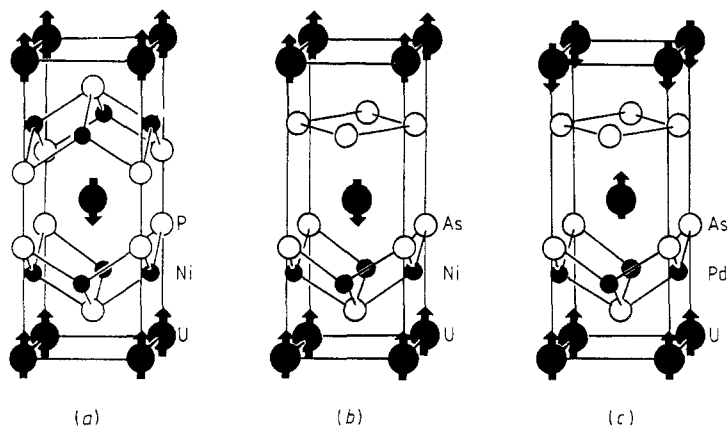
Figure 3. Crystal and magnetic structures of (a) UNi_2P_2, (b) $UNiAs_2$ and (c) $UPdAs_2$. Arrows indicate the alignment of magnetic moments.

cell is tetragonal and doubled along the c direction compared with the chemical cell. The absence of the magnetic reflection (001) proves that the magnetic moments are aligned along the four-fold axis. According to the observed magnetic intensities the sequence of ferromagnetic sheets is $++--\ldots$, as shown in figure 3. The intensities of magnetic peaks as a function of the magnitude of the momentum transfer Q decrease in approximate accordance with a squared U^{4+} or U^{3+} form factor (Freeman *et al* 1976). Our
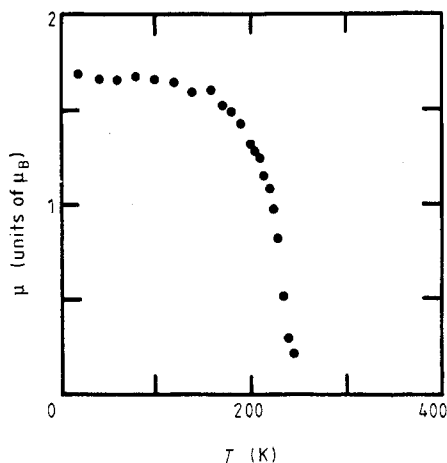
Figure 4. The temperature variation of the ordered magnetic moment of U in UPdAs₂ determined from the variation of the M(101) peak intensity versus T.

results, based on intensities of 12 single magnetic reflections, indicate that only the uranium atoms carry localised magnetic moments. The ordered moment of uranium at 8.7 K amounts to $1.69(5)\mu_B$. The variation of the M(101) peak intensity versus temperature yielded a Néel point T_N of 235 K (see figure 4).

4. Discussion

It is worthwhile noting that an increase in the magnetic susceptibility at low temperature observed in UPdAs₂ is characteristic of the semimetallic uranium antiferromagnets of UX_2 type (X = P, As, Sb, Bi) (Troć 1987). Likewise, the same feature was observed in the $\chi(T)$ curve measured on both the powder and single-crystal specimens of antiferromagnetic $U_4Cu_4P_7$ phosphide (Kaczorowski and Troć 1987). Therefore it is not possible to exclude the possibility that the above phenomena might originate from crystal field effects, as in the case of the cerium monopnictides (Wang and Cooper 1970).

The near-neighbour coordination of the uranium atoms in UPdAs₂ is of C_{4v} symmetry. The Pd and As II atoms are localised at crystallographically equivalent positions. The coordination sphere for the palladium atoms consists of 12 nearest neighbours (4Pd, 4U and 4As II), forming an irregular icosahedron. The coordination number for the As I and As II atoms is eight. The calculated interatomic distances are listed in table 2. It is seen that the large U–U separation precludes any direct exchange interaction and favours both indirect exchange via large ions such as As and RKKY-type interactions via conduction electrons.

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