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Antiferromagnetic Structure of Uranium Diphosphide

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The antiferromagnetic structure of tetragonal UP_2 below the Néel temperature (203 °K) is determined by neutron diffraction with polycrystalline samples. The magnetic unit cell is twice the size of the chemical one along the *c*-axis. The magnetic structure consists of ferromagnetic sheets of uranium stacked along the *c*-axis in the order $+ - - +$. The magnetic moments of the uranium are parallel to the *c*-axis; their magnitude is (1.0 ± 0.1) BM.

Die antiferromagnetische Struktur von tetragonalem UP_2 unterhalb der Néel-Temperatur (203 °K) wird durch Neutronenstreuung an polykristallinen Proben bestimmt. Die magnetische Einheitszelle hat die doppelte Größe der chemischen längs der *c*-Achse. Die magnetische Struktur besteht aus ferromagnetischen Lagen von Uran, die entlang der *c*-Achse in der Folge $+ - - +$ gestapelt sind. Die magnetischen Momente des Urans sind parallel zur *c*-Achse; ihre Größe ist $(1{,}0 \pm 0{,}1)$ BM.

1. Introduction

Antiferromagnetism has been recently discovered in a number of uranium compounds with the Cu_2Sb and PbFCl types of crystal structure [1, 2, 3, 4]. The ordering of the magnetic moments in antiferromagnetic uranium oxysulphide UOS was determined by Ballestracci et al. [3] by the neutron diffraction method. Similarly the antiferromagnetic structures of uranium oxytelluride UOTe [5] and uranium diarsenide UAs_2 [6] were also studied by this method.

From the $1/\chi$ vs. temperature curve in the temperature range between liquid nitrogen and room temperatures it was concluded that below 203 °K UP_2 is antiferromagnetically ordered. The paramagnetic moment above this temperature was determined to be 2.30 Bohr magnetons. Recently, these measurements have been extended up to 430 °K and from the plot of $1/\chi$ vs. temperature is evident that a slope at about 293 °K exists. The paramagnetic moment above this temperature increases to 2.50 BM and the Weiss constant is +30 [7].

A neutron diffraction study of UP_2 at room and liquid nitrogen temperatures has been undertaken with the aim of determining the alignment of the magnetic moments in the antiferromagnetic state, in order to determine the average value of the magnetic moment and to obtain the magnetic form-factor curve for uranium. Apart from this the crystal structure of UP_2 has been checked again, as for neutrons the ratio of scattering amplitudes of uranium and phosphorus is more favourable than in the case of X-rays.

2. Crystallographic Data

UP_2 was prepared in powder form by heating calculated amounts of uranium powder and red phosphorus during 24 hours at 400 °C in vacuo. The sample was then homogenized during one week at 800 °C.

The following values of the lattice constants were obtained with CuK_α radiation: $a = 3.810 \pm 0.005$ Å, $c = 7.764 \pm 0.005$ Å, $c/a = 2.03$. Only the diffraction lines belonging to UP_2 appeared on the X-ray diagram.

UP_2 was reported to be tetragonal, Cu_2Sb type of crystal structure (C38) with two UP_2 units per cell [8]. The space group is $P4/nmm - D_{4h}^7$ (No. 129). The U atoms were placed in the (c) sites:

$$2\ \text{U in (c):} \quad 1/4,\ 1/4,\ u;\ 3/4,\ 3/4,\ \bar{u};$$

with $u = 0.280 \pm 0.001$.
The P atoms were placed as follows:

$$2\ \text{P I in (a):} \quad 3/4,\ 1/4,\ 0;\ 1/4,\ 3/4,\ 0;$$

$$2\ \text{P II in (c):} \quad 1/4,\ 1/4,\ z;\ 3/4,\ 3/4,\ \bar{z};$$

with $z = -0.365 \pm 0.003$.
(The origin was taken at the centre of symmetry.)
The coordination and interatomic distances in UP_2 are shown in Table 1

Table 1

Atom	Neighbour	C.N.	Distance (Å)
P I	P II	4	3.417
	U	4	2.890
	P I	4	2.694
P II	P I	4	3.417
	U	1	2.756
	U	4	2.774
U	P II	1	2.756
	P I	4	2.890
	P II	4	2.774

Every uranium atom is situated inside a square pyramid built of phosphorus atoms. The observed U-P distance is approximately the sum of ionic radii of U^{4+} (0.97 Å) and P^{3-} (1.86 Å) where $R_U + R_P = 2.83$ Å.

3. Neutron-Diffraction Measurements

Neutron diffraction patterns were obtained using 1.10 Å neutrons from the 4 MW reactor EWA in Świerk. The observed neutron intensities were derived in the usual way. They are compared with the calculated ones in Table 2. For this calculations the z- and u-parameters as quoted above were adopted. No temperature factor was allowed for. For this set the conventional discrepancy factor is 0.03_5, consequently no further refinement was carried out.

On the neutron diffraction pattern obtained at liquid nitrogen temperature five new peaks of magnetic origin appeared, one of them, M(115), was overlapping with the Al peak due to the sample-holder. The above mentioned peaks were satisfactory indexed on the basis of a new unit cell with a doubled c-parameter. The absence of the M(001) magnetic reflection is an indication that the magnetic moments in UP_2 are aligned along the crystallographic unique axis similarly, as it was found by Oleś in isostructural UAs_2 [6].

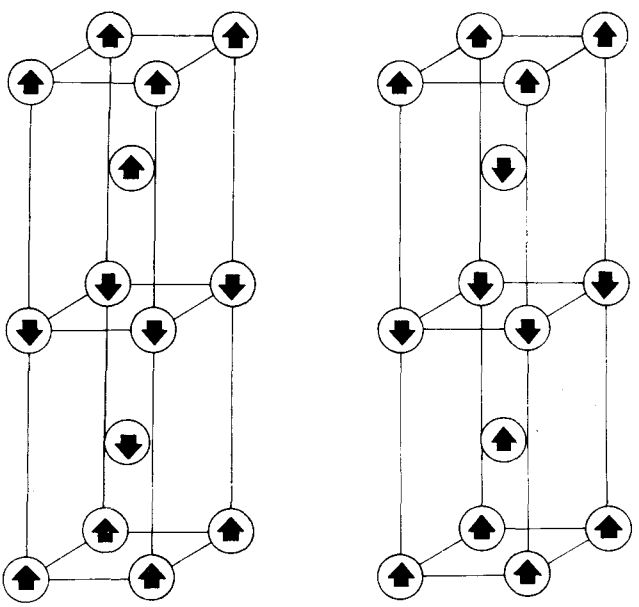
Table 2
The calculated and observed neutron intensities for UP_2

$h\ k\ l$	jF^2_{obs}	jF^2_{calc}
0 0 1	0	0.00
0 0 2	1.3	0.86
1 0 1	6.9	6.16
1 0 2 1 1 0	15	12.9
0 0 3 1 1 1	50	53.1
1 1 2	61	61.0
1 0 3	34	33.2
0 0 4 2 0 0 1 1 3 2 0 1	65	66.2

There are two possible models of the magnetic structure which are illustrated schematically in Fig. 1. The μf values for the four magnetic reflections were calculated for both models.

The calculations for model No. 1 were made on the basis of the space group $P4/nmm$ for a unit cell with four uranium atoms distributed in two (c) sites each with different u-values:

$$u_1 = 0.140 \quad \text{and} \quad u_2 = 0.640.$$



a b

Fig. 1. Two possible models of the magnetic moment alignment in UP_2;
a) the + − − + sequence of ferromagnetic sheets discovered in UP_2,
b) the + + − − sequence found in UOS [3]

Table 3

The μf values calculated for two possible models of the moment alignment in UP_2. Indexing on a doubled unit cell

$h\ k\ l$	μf for model No. 1	μf for model No. 2
M 1 0 1	0.82	0.89
M 1 0 3	0.66	0.41
M 1 0 5 / 1 1 3	0.65	2.67
M 2 0 3	0.52	1.07

The adaption of model No. 2 requires the space group of lower symmetry but with the same extinction rule. The space group $P4$ was taken for calculations and the U atoms were placed in two 1 (a) sites with $u_1 = 0.140$, $u_2 = 0.640$, and in two 1 (b) sites with $u_3 = 0.360$, $u_4 = 0.860$.

It follows from Table 3 that more reasonable results are provided by model No. 1 in which the uranium moments are distributed in sheets parallel to the (001) plane. The magnetic ordering within each sheet is ferromagnetic. The sequence of sheets in the direction of the fourfold axis is $+\ -\ -\ +$ as compared to the $+\ -\ \ldots$ sequence in UOTe and $+\ +\ -\ -$ in UOS. Such a sequence of the sheets can be related to the sign of the Weiss constant for UOS, UOTe, and UP_2. This is shown in Table 4.

Table 4

No.	Compound	Sequence	Parameter u	Weiss const.	Magnetic moment	Reference
1	UP_2	$+\ -\ -\ +$	0.280	+86	1.0	this paper
2	UAs_2	$+\ -\ -\ +$	0.283	+34	1.6	[6, 2]*)
3	UOS	$+\ +\ -\ -$	0.199	−51	1.9	[3]
4	UOTe	$+\ -\ \ldots$	0.175	−56	2.1	[5, 4]

*) In [6] the sequence of ferromagnetic sheets in UAs_2 is incorrectly given as $+\ +\ -\ -$.

Each U atom within a ferromagnetic sheet is sorrounded by four neighbours at a distance 3.810 Å. The closest distance between the U atoms belonging to two antiferromagnetically coupled sheets is 4.351 Å, whereas the U-U distances between neighbouring ferromagnetic sheets is 5.115 Å.

The magnetic form factor curve has been constructed using the data obtained from the intensities of four magnetic reflections. The points obtained from this powder data fit very well to the curve determined previously by Oleś [6] for UAs_2. More detailed data about the form factor for U^{4+} in UO_2 as well as for UN, obtained by single-crystal study, have been published recently [9, 10, 11].

The results of the present study for powdered UP_2 are in very good agreement in the angular range examined with the single-crystal measurements for U^{4+}. It is evident from papers quoted above that the form factor of U^{4+} has 5f cha-

racter, because it diminishes too slowly with increasing sin θ/λ to be explained by a 6d configuration. Therefore it was concluded that a 5f outer-electron at an uranium atom is present in UP_2.

The magnetic moment of the uranium atom in UP_2 was derived by extrapolating μf to zero angle. The value of μ was found to be 1.0 ± 0.1 BM, which was suprisingly small in comparison with the theoretical value expected for a $5f^2$ configuration ($g J = 3.20$ BM). A still lower value of the magnetic moment was found in the case of UN (0.75 BM) [11].

One should not expect, however, to find a maximum value for the magnetic moment in the solid, because the ground state $^3H_4$ will be in this case probably split by the crystal field.

Hutchison and Candela [12] and Ayant et al. [13] have calculated the effect of the crystalline field on the 5f electrons in U^{+4} ions for UO_2 and UOS, respectively. They have found that the influence of the crystal field results in a decrease of the value of the magnetic moment in the paramagnetic range. This has been also observed in the case of UP_2: the experimentally determined value is 2.30 BM as compared to the calculated value for the $5f^2$ structure amounting to 3.58 BM. One should expect that also in the antiferromagnetic range the effect of the crystal field diminishes the value of the magnetic moment of uranium in UP_2 similarly as in the case of other compounds of uranium (Table 4).

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