

## The magnetization density in a $\text{UCu}_2\text{P}_2$ single crystal

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 8877

(<http://iopscience.iop.org/0953-8984/6/42/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 20:51

Please note that [terms and conditions apply](#).

## The magnetization density in a $\text{UCu}_2\text{P}_2$ single crystal

A Delapalme†, Z Żolnierek‡, R Troć‡ and D Kaczorowski‡

† Laboratoire Leon Brillouin, CEA/CNRS, CE-Saclay, 91191 Gif-sur-Yvette, France

‡ W Trzebiatowski Institute for Low-Temperature and Structural Research, Polish Academy of Sciences, 50-950 Wrocław, PO Box 937, Poland

Received 5 April 1994, in final form 16 June 1994

**Abstract.** Using polarized neutrons we have studied the magnetization density arising from unpaired electrons in the compound  $\text{UCu}_2\text{P}_2$ . This phosphide crystallizes in the hexagonal  $\text{CaAl}_2\text{Si}_2$ -type structure ( $P\bar{3}m1$ ) and is a ferromagnet with the highest Curie temperature ( $T_c = 216$  K) among all known  $5f$ -electron compounds. Analysis of the experimentally derived form-factor function  $f(\sin\theta/\lambda)$  indicates an admixture of the  $6d$  states with the  $5f$  states due to the overlapping and covalency effects. In addition, we have found that this form factor is affected by the crystal-field effect occurring either for the  $\text{U}^{4+}$  or  $\text{U}^{3+}$  ion. In agreement with the molecular approach developed by Watson and Freeman to correlate covalency with magnetization density, we found a real occupation of the  $6d$  states with the spatial symmetry of the U site, which explains an important anisotropy of the magnetic form factor at low values of  $\sin\theta/\lambda$ .

### 1. Introduction

The  $f$ -electron elements, i.e. rare earths (RE) and actinide (An) series, form the largest family among ternary intermetallics of general formula  $(\text{RE}, \text{An})\text{T}_2\text{M}_2$ , where T stands for a transition metal and M is a main group element, such as Si, Ge, Sn, P, As and Sb. The majority of the  $(\text{RE}, \text{An})\text{T}_2\text{M}_2$  ternary compounds crystallize with a tetragonal structure of  $\text{ThCr}_2\text{Si}_2$  type ( $I4/mmm$ ), but some of them adopt the  $\text{CaBe}_2\text{Ge}_2$ -type lattice ( $P4/nmm$ ) and there are just a few phases exhibiting a hexagonal structure of  $\text{CaAl}_2\text{Si}_2$  type ( $P\bar{3}m1$ ). The magnetic and electrical properties in these kinds of compounds are often connected to the complex interactions of the localized magnetic moments of actinide atoms with the conduction electron band. As an example, we mention here the well known heavy-fermion systems such as  $\text{CeCu}_2\text{Si}_2$  and  $\text{URu}_2\text{Si}_2$ , which enhanced the fascinating relationship between heavy-fermion superconductivity and magnetism. Thus,  $\text{UCu}_2\text{P}_2$  is one of the rare representatives of the hexagonal 1:2:2 ternary compounds. Recent extended studies of structural [1], magnetic and electrical [2] as well as optical and magneto-optical [3, 4] properties have shown  $\text{UCu}_2\text{P}_2$  to be a uniaxial ferromagnet with the highest Curie temperature ( $T_c = 216$  K) among all the uranium and transuranium binary and ternary compounds. The positive effect of pressure on  $T_c$  observed in  $\text{UCu}_2\text{P}_2$  [5] supports the localized nature of  $5f$  states in this material. An effective magnetic moment of  $2.26\mu_B$  and  $\theta_p = 212$  K have been reported [2]. From the crystallochemical considerations  $\text{UCu}_2\text{P}_2$  can be thought of as a quasi-ionic compound  $\text{U}^{4+}\text{Cu}_2^+\text{P}_2^{3-}$  with the localized  $5f$  electrons of the  $\text{U}^{4+}$  ion. Under this assumption, Kaczorowski [6] has developed a phenomenological crystal-field approach in order to interpret both the magnetic susceptibility, measured on a single crystal, and the observed value  $\mu_{\text{ord}} = 1.78\mu_B$ . He was able to explain the observed

magnetic properties admitting a doublet as a ground state in  $D_{3d}$  crystal-field symmetry. However, this result seems to be a little puzzling, because six  $P^{3-}$  anions in  $UCu_2P_2$  form a nearly perfect octahedron, for which in the case of  $U^{4+}$  a singlet non-magnetic ground state is expected. On the other hand, a magnetic doublet should be a ground state when the  $U^{3+}$  ion is considered in such a symmetry. As electrical resistivity measurements indicated [2],  $UCu_2P_2$  is semimetallic. Therefore one cannot prejudge whether the  $U^{4+}$  or  $U^{3+}$  ions are responsible for the magnetism in this compound. In order to clarify this problem and the electronic bonding in this compound we have undertaken form factor measurements to disclose from the diffracted magnetic amplitudes with polarized neutrons components of both covalency and crystal-field effects.

## 2. X-ray and neutron crystallographic structure

Single crystals of about  $4 \text{ mm}^3$  were obtained by the chemical vapour transport method using I as a transporting agent in a temperature gradient of  $900\text{--}950^\circ\text{C}$ , as reported previously [1, 2]. The crystals present hexagonal faces perpendicular to the  $\bar{3}$  axis and have a measured density  $d_{\text{exp}} = 8.22 \text{ g cm}^{-3}$ . The crystal structure [1] was determined from single-crystal x-ray diffraction and the results are given in table 1.

**Table 1.**  $UCu_2P_2$ : x-ray crystallographic structure refined with 25 reflections and corresponding isotropic thermal coefficients [1]. The unit cell contains one formula unit.

$a = 3.941(1) \text{ \AA}$	$z(\text{Cu}) = 0.6335(6)$	$B(\text{Cu}) = 0.96 \text{ \AA}^2$
$c = 6.366(2) \text{ \AA}$	$z(\text{P}) = 0.258(1)$	$B(\text{P}) = 0.68 \text{ \AA}^2$
$c/a = 1.615$		$B(\text{U}) = 0.47 \text{ \AA}^2$

$UCu_2P_2$  has a structure with a two-dimensional shape of successive planes of U, P, Cu, Cu, P, U as a sequence along the  $c$  axis of the hexagonal  $\text{CaAl}_2\text{Si}_2$ -type unit cell, which can be regarded as a distorted hexagonal close packing of the Si atoms; the space group is  $P\bar{3}m1$  and the U atom is coordinated by six P atoms forming a nearly perfect octahedron, whereas the Cu atom has almost perfect tetrahedral coordination (figure 1). Because a polarized neutron experiment (PNE) requires precise values of the nuclear structure factor  $F_N$ , we have been obliged to perform a four-circle experiment at the Orphée reactor (5C2;  $\lambda = 0.831 \text{ \AA}$ ) to obtain the anisotropic thermal parameters expressed in terms of the  $\beta_{ij}$  coefficients. The results of the refinement at 300 K for 553 reflections are given in table 2.

**Table 2.** Neutron crystallographic structure refined with 553 reflections from a four-circle experiment at 300 K.  $a = 3.953(1) \text{ \AA}$ ;  $c = 6.389(1) \text{ \AA}$ ;  $c/a = 1.616$ ;  $U(0,0,0)$ ;  $\text{Cu}, P(\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, -z)$ ;  $z(\text{Cu}) = 0.6338(1)$ ;  $z(\text{P}) = 0.2565(1)$ ;  $R(F_M) = 2.37\%$ ;  $\eta(\text{mosaic}) = 1.7(1)^\circ$ .

	$\beta_{11} = \beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13} = \beta_{23}$	$\langle u \rangle (\text{Å})$
U	0.0085(3)	0.0023(1)	0.0042(1)	0	0.065
Cu	0.0171(3)	0.0042(1)	0.0085(2)	0	0.097
P	0.0111(3)	0.0028(1)	0.0055(1)	0	0.077

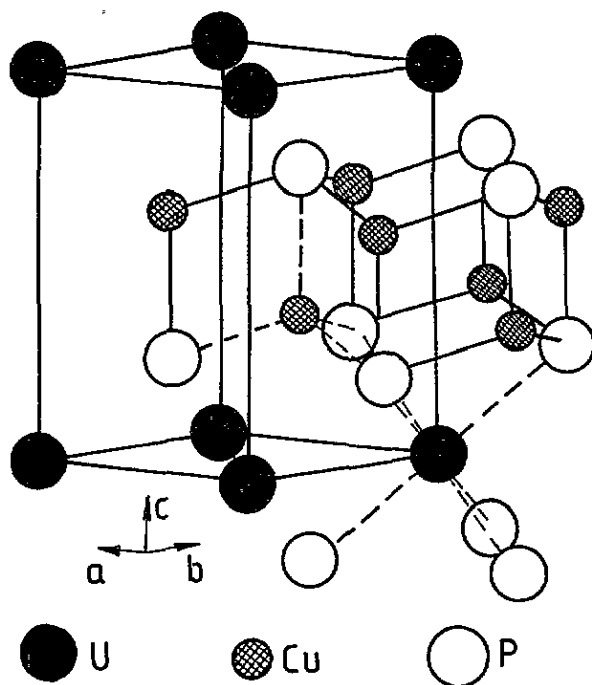


Figure 1. The crystal structure of  $UCu_2P_2$ : ----, coordination polyhedra of the U and Cu atoms.

It is worth noting that although the  $a$  and  $c$  values differ from those of [1] (perhaps due to an uncertainty in the neutron wavelength value) the ratio  $c/a$ , and the  $z(\text{Cu})$  and  $z(\text{P})$  values, are in complete agreement. The refined value of the mosaic yields a 27% level of extinction on the strongest (110) reflection but only a few per cent for the majority of the recorded intensities.

A list of 11 nuclear integrated intensities measured at 10 K gives a result only when constraining the thermal coefficients with the experimental relation  $4\beta_{33} = \beta_{11}$  observed at 300 K; the refined crystallographic parameters are  $a = 3.92(1)$  Å and  $c = 6.33(2)$  Å and the resulting  $\beta_{ij}$  coefficients have been used to process the polarized neutron data. With these values of  $a$  and  $c$  parameters, one has an octahedron of P atoms for the U site with two P–P distances (3.92 Å and 3.96 Å), and the Cu atoms are coordinated by four P atoms forming a tetrahedron slightly elongated along the  $c$  axis (Cu–P, 2.37 Å and 2.39 Å) (figure 1). The calculated U–P distance is 2.79 Å with an equivalent isotropic displacement  $\langle u \rangle = 0.065$  Å for the U atom.

### 3. Polarized neutron experiment (PNE)

A PNE has been carried out on the 5C1 instrument of the Orphée reactor with a wavelength  $\lambda = 0.86$  Å. The mosaic spread ( $1.7^\circ$ ) was obtained from the refinement of the four-circle data.

Due to the probable formation of very narrow Bloch walls, the occurrence of a large domain effect is expected [2] when one examines the magnetization curve versus temperature with an applied field (field cooled) and without an applied field (zero-field cooled); under

small magnetic fields it shows the typical shape of a ferromagnet with strong domain effect. Therefore, we measured, at 10 K, 45 inequivalent flipping ratios under a magnetic field of 3.5 T applied along the  $c$  axis: reflections with  $l = 0, 1, 2$  were recorded for values of  $\sin\theta/\lambda$  ranged between 0.1 and  $1.0 \text{ \AA}^{-1}$ . Due to the high symmetry, many equivalent flipping ratios (ratios of the diffracted intensities with incident neutron spins up and down) were measured for each inequivalent reflection.

The flipping ratio  $r(hkl)$  in the case of a centrosymmetric collinear ferromagnet is given by the relationship

$$r(hkl) = \frac{F_N^2 + q^2 F_M^2 + 2q^2 F_N F_M}{F_N^2 + q^2 F_M^2 - 2q^2 F_N F_M} \quad (1)$$

where  $F_N$  and  $F_M$  are the expressions for the nuclear and magnetic structure factors, respectively, and  $q^2 = \sin^2(Q, M)$  with  $M$  the direction of the magnetic moments and  $Q$  the wave-vector.

After a more precise examination of the reflections (111), (112), (301) and (302) for control of the  $\gamma (= F_M/F_N)$  values deduced from  $r(hkl)$  (1) we confirmed the precedent values of the flipping ratios but we eliminated those reflections that gave unreliable magnetic amplitudes due to the very small value of  $F_N$  ( $|F_N| < 0.4 \times 10^{-12} \text{ cm}$ ). Indeed the derivative of the  $\gamma$  expression leads to a standard error  $\sigma(F_M) = F_M[\sigma^2(F_N)/F_N^2 + \sigma^2(\gamma)/\gamma^2]^{1/2}$ , which is proportional to  $F_M$  and mainly driven by  $\sigma(F_N)/F_N$  in the case of a low value of  $F_N$ . For these reflections, small deviations of  $z(\text{P})$ ,  $z(\text{Cu})$  or  $\beta_{ij}$  yield an important relative change of calculated  $F_N$  and then of the corresponding magnetic structure factor  $F_M$ , which becomes unreliable for testing any magnetic model of structure. The measured magnetic amplitudes are gathered in table 3 and in figure 2. Due to the special position (0,0,0) of the U atom in the unit cell and very small magnetic moments residing on the Cu and P atoms, the magnetic amplitudes may follow the U form factor with some deviations due to covalency at low  $\sin\theta/\lambda$  and due to crystal field and covalency effects at high values of  $\sin\theta/\lambda$ .

These effects can be inferred from the analysis of the magnetic structure factor  $F_M$

$$F_M(Q) = 0.2695 \sum_i \mu_i f_i(Q) \exp(iQ \cdot r_i) \exp(-W_i) \quad (2)$$

where the sum extends over all magnetic atoms in the unit cell with positions  $r_i$  and the respective Debye-Waller factors  $W_i$ . In (2),  $\mu_i$  represents a magnetic moment in Bohr magnetons and  $f_i(Q)$  is the so-called magnetic form factor defined for the f-electron system as

$$f_i(Q) = \langle j_0 \rangle + C_2 \langle j_2 \rangle + C_4 \langle j_4 \rangle + C_6 \langle j_6 \rangle. \quad (3)$$

In the above formula the  $\langle j_k \rangle$  are the one-electron radial integrals

$$\langle j_k \rangle = \int_0^\infty \rho(r) j_n(Qr) 4\pi r^2 dr \quad (4)$$

and the  $C_k$  coefficients are the products of special tensor operators [7, 8] taken over the  $|LSJM_J\rangle$  ground state of the free magnetic ion. In the simplest approach one uses the  $\rho(r)$  density determined for a free-ion wavefunction and the  $C_k$  coefficients are derived for its ground state  $|LSJM_J = J\rangle$ . Such quantities for various free ions,  $U^{3+}$ ,  $U^{4+}$  and  $U^{5+}$ , have already been calculated by Freeman and Desclaux [9, 13].

In a real crystal the respective  $C_k$  coefficients and  $\langle j_k \rangle$  integrals may be modified by the following effects. The crystal-field effect and/or the  $jj$  coupling will modify the  $C_k$  values since the ground state of a magnetic ion in a solid is a combination of different  $|LSJM_J\rangle$  states. The free ion  $\langle j_k \rangle$  integrals involved in the 5f-electron density  $\rho(r) = \varphi(5f)\varphi^*(5f)$  are affected in a crystal by the overlapping and covalency effects induced by the surrounding ligands. The latter effects were discussed by Watson and Freeman [10].

Table 3. Magnetic amplitudes observed and calculated in the case of  $\bar{3}m$  symmetry applied on U(6d) and cubic symmetry applied on Cu(3d).

$h$	$k$	$l$	$\sin \theta/\lambda$	$F_M$ (observed)	$F_M$ (calculated)	$\sigma$
1	0	0	0.147	1.785	1.721	13
1	0	1	0.167	1.653	1.678	9
0	1	1	0.167	1.733	1.753	10
0	1	2	0.216	1.676	1.655	17
1	1	0	0.255	1.329	1.315	9
2	0	0	0.295	1.142	1.207	13
2	0	1	0.305	1.174	1.176	8
0	2	1	0.305	1.147	1.143	8
2	0	2	0.334	1.108	1.052	20
2	1	0	0.390	0.885	0.884	9
2	1	1	0.398	0.837	0.843	10
1	2	1	0.398	0.844	0.852	8
1	2	2	0.420	0.761	0.751	10
3	0	0	0.442	0.717	0.717	12
2	2	0	0.510	0.544	0.541	13
3	1	1	0.537	0.493	0.462	10
1	3	1	0.537	0.472	0.477	10
3	1	2	0.554	0.436	0.423	15
4	0	1	0.594	0.349	0.362	9
0	4	1	0.594	0.371	0.334	19
0	4	2	0.610	0.329	0.312	22
3	2	1	0.647	0.320	0.278	12
2	3	1	0.647	0.268	0.242	19
2	3	2	0.661	0.234	0.240	15
4	1	0	0.675	0.269	0.248	12
5	0	1	0.741	0.193	0.139	22
0	5	1	0.741	0.192	0.186	32
5	0	2	0.753	0.138	0.163	31
3	3	0	0.765	0.175	0.171	15
4	2	1	0.783	0.166	0.098	20
2	4	1	0.783	0.137	0.150	18
4	2	2	0.795	0.149	0.128	20
5	1	1	0.824	0.147	0.130	22
1	5	1	0.824	0.117	0.074	22
1	5	2	0.835	0.091	0.108	20
6	0	0	0.884	0.091	0.108	23
4	3	1	0.899	0.102	0.098	16
3	4	1	0.899	0.113	0.039	18
3	4	2	0.910	0.074	0.082	26
5	2	0	0.920	0.115	0.097	17
6	1	1	0.969	0.102	0.022	24
1	6	1	0.969	0.084	0.081	43

## 4. Data analysis

### 4.1. Overlapping and covalency in the molecular approach

According to the formalism developed by Watson and Freeman [10], the electron density  $\rho'(\mathbf{r})$  for a magnetic ion imbedded in a crystal can be expressed as

$$\rho'(\mathbf{r}) = |\varphi|^2[1 - (\delta^2 - S^2)] + |\Lambda|^2(S + \delta)^2 - 2\varphi\Lambda(S + \delta) \quad (5)$$

where  $\varphi$  denotes one of the U orbitals and  $\Lambda$  refers to an occupied pair of ligand orbitals. In general, the orbitals  $\varphi$  and  $\Lambda$ , appropriate to the free ions and centred at different sites, are

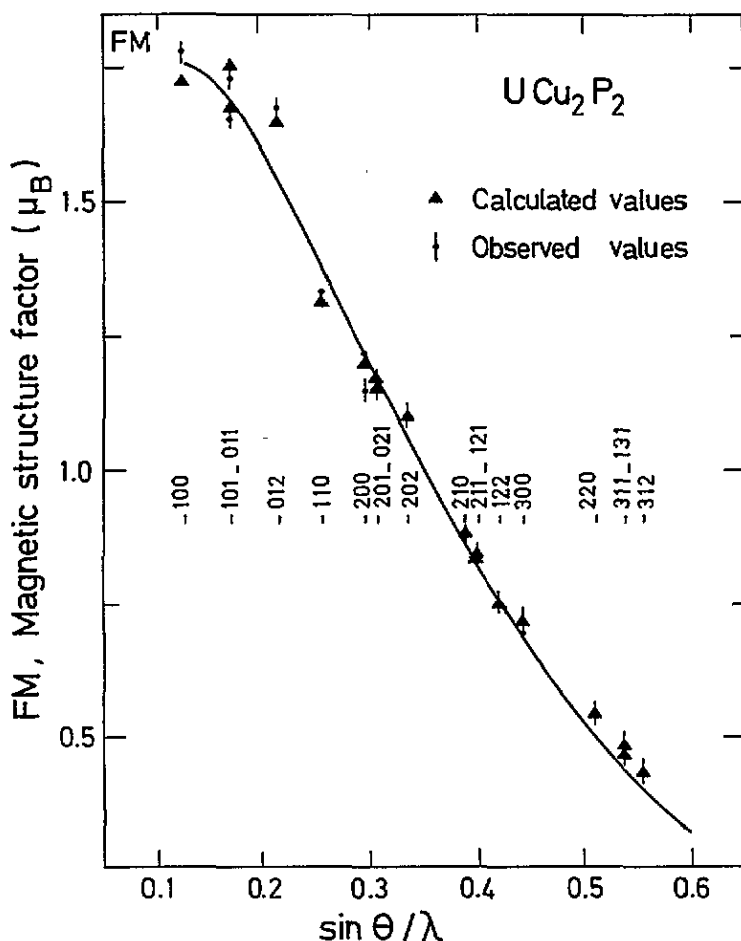


Figure 2. The calculated and observed magnetic amplitudes for reflections drawn from table 3 and with  $\sin \theta / \lambda < 0.55 \text{ \AA}$ ; a many-monopolar model can explain the splitting of reflections (101) and (011) but not the values observed for the (012) and (110) reflections.

not orthonormal, so  $S = \langle \varphi | \Lambda \rangle$  defines an overlap integral. In addition, due to the electron transfer from the ligand to the metal site the covalency effect occurs. This means that the pure  $\varphi$  orbital should be replaced by a quantum-mechanical mixture  $(\Lambda + \delta\varphi)$ , where  $\delta$  is called the covalency factor, which will consequently influence the magnetic amplitudes that we measure in a PNE. When the  $\delta$  and  $S$  values are not known *a priori*, the real  $\rho'(r)$  value can be modelled in an approximate way by expanding  $\rho'(r)$  in a multipole series

$$\rho'(r) = P_{\text{val}} \rho_{\text{val}}(r) + \sum_{l=0}^4 R_l(r) \sum_{m=0}^4 P_{lm\pm} Y_{lm\pm} \left( \frac{r}{r} \right) \quad (6)$$

where  $\rho_{\text{val}}$  is the spherical Hartree-Fock valence density with weight  $P_{\text{val}}$ ,  $Y_{lm\pm}$  are spherical harmonics in the real form with weight  $P_{lm\pm}$  and  $R_l(r)$  represents the radial part of the multipole functions. (6) is the basis for a least-squares program in which  $P_{\text{val}}$  and  $P_{lm\pm}$  are determined [11, 12].

In the program MOLLY, we have used for the U atom of the  $U^{3+}$  and  $U^{4+}$  form factors calculated by Desclaux and Freeman [13]; furthermore we remark that the spherically symmetric component of the ionic form factor of  $U^{3+}$  (or  $U^{4+}$ ) is well known and contains no adjustable parameters, so that deviations from the spherical model are reliable.

The usefulness of functions simpler than Hartree-Fock functions was recognized long ago, especially for those problems where high accuracy is not required. For the 3p electrons of the P atom and the 3d electrons of the Cu atom, we have used a single-exponential function to describe an atomic orbital as Zener [14] and Slater [15] pointed out in their early papers. On the one hand Roothaan [16] has developed a self-consistent-field method to characterize the one-electron function of an electron in an atomic system; on the other hand Clementi and Roetti [17] as well as McLean and McLean [18] presented tables of the exponents of the basis functions and the coefficients to be used in analytical wave-functions  $\varphi(e)$  expanded in the Roothaan-Hartree-Fock method. They gave the analytical expression

$$\varphi(e) = \{(2\xi)^{n+1/2}/[(2n)!]^{1/2}\}r^{n-1}\exp(-\xi r). \quad (7)$$

Physically, the orbital exponent  $\xi$  of such functions is  $\xi = (Z - s)/\nu$ , where  $(Z - s)$  is the effective nuclear charge for a given electron ( $s$  is the screening constant), and  $\nu$  is a function of the principal quantum number.

The maximum of the radial charge density is obtained by the radial derivative of the quantity

$$\varphi = 4\pi r^2 \varphi \varphi^* \propto r^2 r^{2(n-1)} \exp(-2\xi r)$$

and one deduces easily  $r_{\max} = n/\xi$ .

We have obtained the maximum of the radial charge density for U(5f), U(6d), P(3p) and Cu(3d) orbitals and the various results are gathered in table 4. Although the precise values of these quantities are important for the calculation of atomic equilibrium, in our case only rough estimation of the maximum of the charge density is necessary. The important result is that for the U atom the 5f and 6d electrons have their maxima at very different distances; this property has been used for the characterization of covalent bonding with a U atom.

**Table 4.** Parameters characterizing the atomic orbitals of U, P and Cu derived from the Roothaan-Hartree-Fock method.

	$2\xi$ (au <sup>-1</sup> )	$r_{\max}$ (Å)
U(5f)	7.01	0.71
U(6d)	3.52	1.42
P(3p)	3.26	0.92
Cu(3d)	8.8	0.45

#### 4.2. Magnetization density analysis

To the first approximation  $UCu_2P_2$  may be treated as a quasi-two-dimensional magnetic system. Magnetic properties [2] reveal that this compound orders below 216 K and is a strongly anisotropic ferromagnet with the easy magnetization direction being along the crystallographic  $c$  axis; the transverse component of the spontaneous magnetic moment is found equal to zero. We summarized in table 3 the magnetic amplitudes observed in the experimental conditions:  $0.1 \text{ \AA}^{-1} < \sin \theta/\lambda < 1.0 \text{ \AA}^{-1}$ ;  $l = 0, 1, 2$ .



After suitable corrections for imperfect polarization,  $\lambda/2$  component and extinction, we are left with a set of magnetic amplitudes  $F_M$  corresponding to 42 inequivalent reflections with a good accuracy. In this kind of study, a magnetization density map should be particularly helpful to suggest a magnetic model. Figure 3 shows the Fourier transform of the observed magnetic amplitudes given in table 3 and corresponds to the magnetization density in the (001) plane at different levels. Indeed the precision is good enough in this plane to permit us to say that there is no evident anisotropic effect on the U atom. For the Cu site, a one-contour signal, which is different at the positions  $(\frac{1}{3}, \frac{2}{3}, z)$  and  $(\frac{2}{3}, \frac{1}{3}, z)$ , suggests that a small magnetic moment is present on the Cu atom. However, the lack of many reflections at low values of  $\sin \theta/\lambda$  (reflections with  $l > 2$ ) does not permit us to evaluate either the amplitude or the sign of this magnetic moment. In this case the use of maximum-entropy methods [19] should overcome this kind of difficulty.

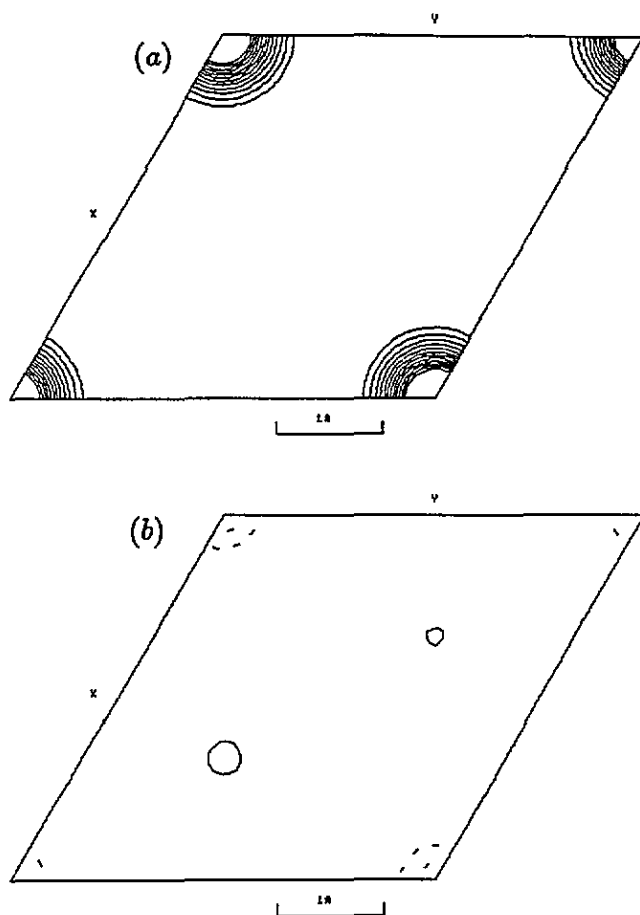


Figure 3. The Fourier transform of the observed magnetic amplitudes of table 3; contours represent  $0.02\mu_B \text{ \AA}^{-3}$ . (a) Section  $z = 0$  showing the U atoms; (b) section  $z = 0.366$  showing the Cu site  $(\frac{2}{3}, \frac{1}{3}, z)$ .

A number of different models have been refined. To test the refinements, we compared the residue of the  $F_M$  refinement, i.e.  $R(F_M)$ , the weighted residue  $R_w$  and the  $\chi$  value

( $\chi = [(\sum(F_{M_{obs}} - F_{M_{calc}})^2/\sigma^2)/(N - p)]^{1/2}$ ;  $N$  is the number of observations and  $p$  the number of parameters), numbers that have been written in the form [ $R(F_M)$ ,  $R_w$ ,  $\chi$ ]. To test the significance of these refinements, we have used Hamilton's criterion on  $R_w$ , which takes account of the fact that as parameters are added, the least-squares refinement improves the agreement between observed and calculated values [20].

The first refinement was restricted to a spherical component on atomic sites—a monopolar model. Comparing the refinements with a spherical magnetic density on the U atom only and on U, Cu, P atoms—a many-monopolar model—we found that a many-monopolar model is probable at the 0.69 level (table 5, columns I and II). Indeed, the splitting of the magnetic amplitudes for the reflections  $hkl$  and  $khl$  (figure 2) is an experimental proof of the presence of magnetic moments on Cu (or P) atoms. Although a many-monopolar model seems to take account of a splitting of the reflections (101) and (011), it cannot explain the observed magnetic amplitude of the reflections (012) and (110).

**Table 5.** Results of refinements; magnetic moments are in  $\mu_B$ . I, monopolar model with magnetic moment on U atom only; II, many-monopolar model with moments on U, Cu, P atoms; III,  $\bar{3}m$  symmetry applied on U(6d) electrons; IV,  $3m$  symmetry applied on Cu(3d) electrons; V,  $\bar{3}m$  symmetry applied on U(6d) and  $3m$  on Cu(3d) electrons; VI,  $\bar{3}m$  symmetry applied on U(6d) and cubic on Cu(3d) electrons.  $p_{BH}$  means Hamilton's criterion level; the columns III and IV are compared to the solution of column II, and the columns V and VI are compared to the solution of column III.

	I	II	III	IV	V	VI
$R(F_M)$	8.07	7.87	5.43	5.81	4.33	4.27
$R_w$	4.85	4.71	3.23	3.99	2.68	2.71
$\chi$	3.66	3.64	2.64	3.21	2.29	2.28
$p_{BH}$		0.69	0.99	0.98	0.99	0.99
$p$	1	3	7	6	10	9
U(5f)	1.98(2)	1.99(2)	2.08(3)	1.99(2)	2.08(2)	2.08(2)
U(6d)	—	—	$< \sigma$	—	$< \sigma$	$< \sigma$
Cu	—	$< \sigma$	-0.01(1)	-0.02(1)	-0.02(1)	-0.02(1)
P	—	0.03(3)	0.03(2)	$< \sigma$	$< \sigma$	0.02(2)

Despite the layered character of the crystal structure (the U-U separation in the  $c$  direction being as large as 6.33 Å), the local coordination around the U (octahedra [UP<sub>6</sub>]) and Cu (tetrahedra [CuP<sub>4</sub>]) atoms is nearly cubic but, for the atomic density, is of  $D_{3d}$  and  $C_{3v}$  point symmetry, respectively. It is worth noting here that the symmetry of the magnetization density can be different from that of crystal-field effects. Indeed, the magnetization density must obey the crystallographic point symmetry of the site, i.e.  $\bar{3}m$  for the U atoms and  $3m$  for the Cu atoms; in the opposite, crystal-field ground state is driven in the zero-order approximation by a nearly cubic symmetry for the U and Cu sites and in the first-order approximation by a trigonal distortion.

To advance further we need to develop a constrained model using the symmetry of the  $UCu_2P_2$  cluster in the unit cell. The f electrons are described with the octopole population; an important result is that a refinement of the octopole population is not possible for the U atom (U:0,0,0; matrix singularity) and leads to a spherical 5f magnetization density for the U atom. Thus, following the analysis of Watson and Freeman [10], we turned towards the d orbitals and looked at the allowed multipole functions describing the d-orbital density in  $\bar{3}m$  (or  $3m$ ) and cubic symmetries. We found that the  $\bar{3}m$  and  $3m$  symmetries ask for (00), (20), (40), (43<sub>+</sub>) multipole functions and the cubic symmetry implies the use of the cubic harmonic K4: (00), (40) + 0.74(44<sub>+</sub>) [21].

If a deformation of the magnetic density with the cubic symmetry has to be rejected [7.89, 4.69, 3.78] for the U(6d) electrons, a  $\bar{3}m$  symmetry gives a net improvement of  $R_w$  (table 5, column III) with a probability at the 0.99 level. The  $3m$  or cubic symmetry on the Cu atom also gives a good improvement of  $R_w$  (table 5, column IV) and the final result is shown (table 5, columns V and VI) with  $\bar{3}m$  symmetry on U(6d) and  $3m$  or cubic symmetry, respectively, on Cu(3d). The observed magnetic moment on the U atom for this solution is  $2.08(2)\mu_B$ , which is high, but definitively below the value of  $3.27\mu_B$  (or  $3.20\mu_B$ ) for the U  $5f^3$  (or  $5f^2$ ) free-ion ground state; the magnetic moment on the Cu atom is refined as  $-0.02(1)\mu_B$ , which is nicely of the same sign as the 6d transferred moment on the U site, and the magnetic moment of P atom lies inside the error bar.

We cannot decide from the values of the residue whether the deformation of the Cu(3d) electrons has  $3m$  or cubic symmetry, but we can say that the refined parameters of the 3d multipoles are better drawn from the cubic solution than those derived from the  $3m$  solution with a smaller number of parameters. In fact we believe that the Cu site is more cubic than the U site with respect to the presence of the four threefold axes. Table 3 gives the observed and calculated magnetic amplitudes corresponding to the case of table 5, column VI; the agreement is surprisingly good especially when comparing the observed and calculated values of reflections (101), (011), (012) and (110).

The last point is difficult to specify: which is the real U form factor we have to use in our calculation? To clarify this problem we compared  $R(F_M)$ ,  $R_w$  and  $\chi$  for the solutions of table 5, column V, using the  $U^{3+}$  or  $U^{4+}$  form factors in the cases of intermediate coupling or Russell–Saunders coupling. The result is that the  $U^{3+}$  Russell–Saunders coupling (4.33, 2.68, 2.29) is better than any intermediate coupling, as well as better than the  $U^{4+}$  Russell–Saunders coupling (4.62, 2.97, 2.57). Moreover, we examined experimentally the flipping ratio, and then the magnetic amplitudes versus temperature of the (101) reflection; the result is shown in figure 4 together with the features of figure 4 taken from [22]. The authors of [22] studied the magnetic ordering in a  $U_4Cu_4P_7$  single crystal by neutron diffraction; they found two uranium sites U(1) and U(2) with totally different thermal dependences. U(1) has been identified as  $U^{4+}$  as in  $UP_2$  and U(2) has been identified as  $U^{3+}$  with a doublet as a crystal-field ground state. In our experiment, the thermal dependence of the (101) reflection is totally comparable with U(2) of [22]. Thus these results may suggest that in  $UCu_2P_2$  the U atom behaves as a  $U^{3+}$  ion in the Russell–Saunders coupling.

#### 4.3. Crystal-field contribution

When we compare the magnetic amplitudes of  $hkl$  and  $khl$  reflections for the many-monopolar model (such as 101 and 011 reflections), we observe a negligible splitting of the calculated magnetic amplitudes at  $\sin\theta/\lambda > 0.6 \text{ \AA}^{-1}$ , but still some discrepancies between the observed and calculated amplitudes. It is important to point out that the magnetic amplitudes calculated within the many-monopolar model align themselves along an isotropic form factor at high values of  $\sin\theta/\lambda$  whereas the data presented in table 3 indicate a sizeable anisotropy of the form factor with respect to the isotropic one. We think that these deviations between the observed and calculated amplitudes can be accounted for with a crystal-field calculation (see for example the case of  $NpAs_2$  reported in [23]) but we have to keep in mind that these deviations in the case of  $UCu_2P_2$  may originate from both crystal-field and covalency effects.

In  $UCu_2P_2$ , the U atom is surrounded by six P atoms, which form a trigonally distorted octahedron; the distortion in fact is very small. The crystal field will favour some orientations of electronic orbitals and then it will lift the degeneracy of the ground state  $J$ . In order to take into account the crystal-field effect we have considered both possible cases

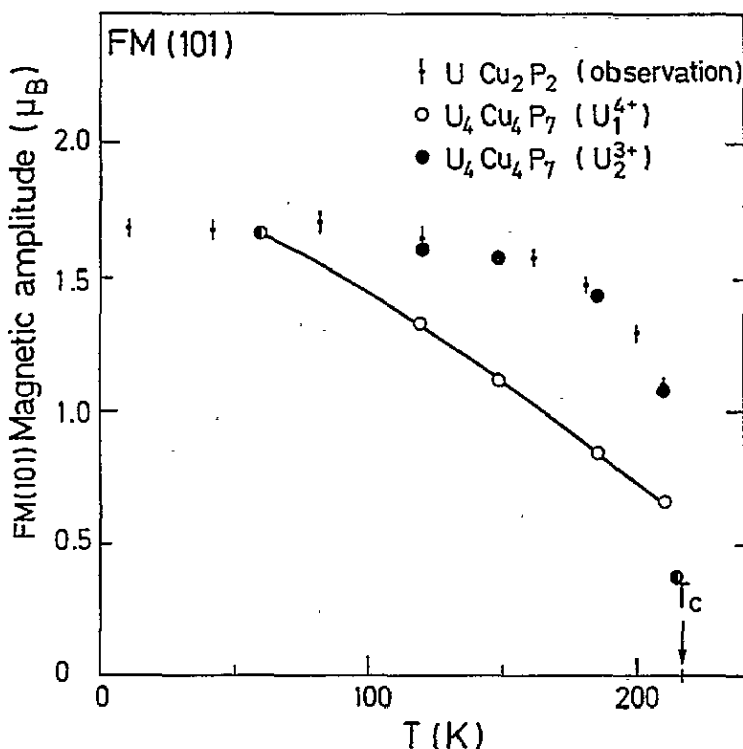


Figure 4. The thermal dependence of the (101) magnetic amplitude compared to the same thermal dependence of the two U sites  $U(1)^{4+}$  and  $U(2)^{3+}$  of the compound  $U_4Cu_4P_7$  reported in [22]. For the sake of clarity, the temperatures and the correspondent magnetic moments observed in  $U_4Cu_4P_7$  [22] have been normalized to the results obtained for the (101) reflection of the  $UCu_2P_2$  compound.

with the  $U^{3+}$  and  $U^{4+}$  ions assuming that a doublet is the crystal-field ground state of U. Since this doublet seems to be well separated from the other crystal-field levels, their wave-functions derived for the paramagnetic state will also be the eigenfunctions in the ordered state. Such an approach is justified by the fact that  $UCu_2P_2$  is a uniaxial ferromagnet with strong exchange interactions ( $T_c = 216$  K) so the relevant experimental conditions, the temperature of measurement (10 K) and the applied magnetic field (35 kOe), will leave the ground state unaffected (isolated and well defined). Therefore we can refine the coefficients of the ground-state wave-function  $|\Psi\rangle = \sum_m a_m |J, m\rangle$  by a calculation of the corresponding magnetic amplitudes and their comparison to the observed ones.

For the  $U^{3+}$  ion, we refined the coefficients of the following trial wave-function:

$$|\Psi_3\rangle = a \left| \frac{9}{2} \right\rangle + b \left| \frac{3}{2} \right\rangle + c \left| -\frac{3}{2} \right\rangle$$

and for the  $U^{4+}$  ion, we refined the coefficients of  $|\Psi_4\rangle$ :

$$|\Psi_4\rangle = a|4\rangle + b|1\rangle + c|-2\rangle$$

(all the coefficients being normalized so that  $a^2 + b^2 + c^2 = 1$ ).

The results show generally a better agreement for  $U^{3+}$  (table 6). A detailed analysis shows that the calculated magnetic amplitude of the (611) and (161) reflections is always

**Table 6.** Amplitudes of the  $|M_J\rangle$  components in the crystal-field ground-state wave-vector for  $U^{3+}$  and  $U^{4+}$  ions.

	$U^{3+}  \Psi_3\rangle$	$U^{4+}  \Psi_4\rangle$
<i>a</i>	0.80(1)	0.85(1)
<i>b</i>	-0.09(9)	-0.04(10)
<i>c</i>	0.59(2)	-0.53(1)
$R_w$	0.0419	0.0487
$m(\mu_B)$	1.72(5)	1.85(3)

equal to zero in the case of the  $U^{4+}$  ion, whereas one observes experimentally a definite value for these two reflections.

These results would be the answer to the question of what the valency of U is in this compound: the low value of the calculated magnetic moment can be explained by the values of the magnetic amplitudes, which are not precise enough at high values of  $\sin\theta/\lambda$ . Although the  $U^{3+}$  hypothesis is more attractive from the point of view of a crystal-field interpretation and the anisotropic molecular-orbital refinement, the possibility of a  $U^{4+}$  ion as supported from electrical and structural considerations cannot be disregarded.

## 5. Conclusions

A polarized neutron experiment has been carried out on a  $UCu_2P_2$  single crystal. The observed magnetic amplitudes showed an important anisotropy at low values of  $\sin\theta/\lambda$ , which can be accounted for on one hand by a magnetic moment on the Cu (or P) atoms, and on the other hand by a deformation of the magnetic density of the 6d and 3d electrons around the U and Cu atoms.

The occupation of the 6d states is proved by the fact that the 5f electrons are found to be spherically distributed and thus the 6d anisotropic density explains the large deviations of magnetic amplitudes of two reflections at low values of  $\sin\theta/\lambda$ .

The authors of [3] and [4] showed by magneto-optical spectroscopy of this compound that  $UCu_2P_2$  is a 'bad' metal with free-carrier concentration below 0.2 carriers/fu, which might permit us to describe it as a semimetal. They concluded that the magnetic moment is associated with the 5f state of the U and, from their magneto-optical data, there is strong evidence of the U  $f \rightarrow Ud$  transition; furthermore, many charge-transfer transitions are assigned to a transition from bonding P(3p) and U(6d) states into empty U(5f) states or from P(3p) states into U(6d,7s) and Cu(4s), yielding more or less compensated band on Cu. Therefore it seems evident that the 6d states play an important role at the U site of this compound, and perhaps this could explain the better agreement we obtained with the  $U^{3+}$  form factor.

## Acknowledgment

The work was partially supported by the KBN grant No 202969101 of the State Council for Scientific Research (Poland).

## References

- [1] Żolnierek Z, Noël H and Kaczorowski D 1987 *J. Less-Common Met.* **128** 265
- [2] Kaczorowski D and Troć R 1990 *J. Phys.: Condens. Matter* **2** 4185
- [3] Schoenes J, Fumagalli P, Ruesegger H and Kaczorowski D 1989 *J. Magn. Magn. Mater.* **81** 112
- [4] Fumagalli P, Schoenes J, Ruesegger R and Kaczorowski D 1988 *Helv. Phys. Acta* **61** 829
- [5] Kaczorowski D, Duraj R and Troć R 1989 *Solid State Commun.* **70** 619
- [6] Kaczorowski D 1988 *J. Magn. Magn. Mater.* **76-77** 366
- [7] Johnston D F 1966 *Proc. Phys. Soc.* **88** 37
- [8] Lovesey S W and Rimmer D E 1969 *Rep. Prog. Phys.* **32** 333
- [9] Freeman A J, Desclaux J P, Lander G H and Faber J Jr 1976 *Phys. Rev. B* **13** 1168
- [10] Watson R E and Freeman A J 1967 *Hyperfine Interact.* ed A J Freeman and B F Frankel (New York: Academic) p 53
- [11] Stewart R F 1976 *Acta Crystallogr. A* **32** 565
- [12] Hansen N K and Coppens P 1978 *Acta Crystallogr. A* **32** 909
- [13] Desclaux J P and Freeman A J 1978 *J. Magn. Magn. Mater.* **8** 119
- [14] Zener C 1930 *Phys. Rev.* **36** 51
- [15] Slater J C 1930 *Phys. Rev.* **36** 57
- [16] Roothaan C C J 1951 *Rev. Mod. Phys.* **23** 69
- [17] Clementi E and Roetti C 1974 *At. Data Nucl. Data Tables* **14** 177
- [18] McLean A D and McLean R S 1981 *At. Data Nucl. Data Tables* **26** 197
- [19] Papoular R J, Ressouche E, Schweizer J and Zheludev A 1993 *Maximum Entropy and Bayesian Methods (Paris, 1992)* ed A Mohammad-Djafari and G Demoment (Dordrecht: Kluwer) p 311  
Papoular R J and Delapalme A 1994 *Phys. Rev. Lett.* **72** 1486
- [20] Hamilton W C 1965 *Acta Crystallogr.* **18** 502-10
- [21] Holladay A, Leung P and Coppens P 1983 *Acta Crystallogr. A* **39** 377
- [22] Burllet P, Troć R, Kaczorowski D, Noël H and Rossat-Mignot J 1994 *J. Magn. Magn. Mater.* **130** 237
- [23] Amoretti G, Blaise A, Bonnet M, Boucherle J X, Delapalme A, Fournier J M and Vigneron F 1982 *J. Physique Coll.* **43 C7** 293