Neutron diffraction study of magnetic structure of U_3Bi_4 and U_3Sb_4

1996 J. Phys.: Condens. Matter 8 10589

(http://iopscience.iop.org/0953-8984/8/49/044)

J. Phys.: Condens. Matter **8** (1996) 10589–10600. Printed in the UK

Neutron diffraction study of magnetic structure of U_3Bi_4 and U_3Sb_4

A Gukasov†, P Wiśniewski†‡§ and Z Henkie‡

† Laboratoire Léon Brillouin (CEA-CNRS), CE Saclay, 91191 Gif sur Yvette, France

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

Received 8 August 1996

Abstract. Experiments using polarized and unpolarized neutrons have been performed on single crystals of U_3Bi_4 and U_3Sb_4.

A magnetic structure with a [001], easy axis and two types of uranium site having different values of the moment was found for both compounds. The values of magnetic moment at these two sites are 2.11 and 1.81 μ_B for bismuthide, and 2.14 and 1.66 μ_B for antimonide.

The appearance of such a structure is ascribed to a low local symmetry of the U-ion environment and hybridization-mediated two-ion interactions.

1. Introduction

U_3Bi_4 and U_3Sb_4 crystallize in the body centred cubic structure (T_d^6 or $I\bar{4}3d$ space group). They are magnetically ordered systems with fairly high Curie temperatures and with strong hybridization of U 5f electrons with conduction band electrons [1, 2]. Another interesting feature of these systems comes from the fact that despite the overall cubic symmetry, the local symmetry of the U-ion neighbourhood is low. This leads to remarkable anisotropic properties (for a review see [3]).

Evidence of the hybridization was found for other compounds of this family U_3P_4 and U_3As_4 by magneto-optical spectroscopy [4] and de Haas–van Alphen measurements [5, 6, 7]. These two compounds have been also investigated by neutron scattering on single crystals [8]. They both are highly anisotropic and have so called non-collinear, three-sublattice magnetic structure with a ferromagnetic component along the [111] direction, as predicted by Buhrer [9] and Przystawa [10].

Further magnetization measurements performed on U_3Sb_4 [1, 11] revealed that it has a net magnetization along the [001] direction which contradicts the three-sublattice model. A collinear magnetic model has therefore been proposed for U_3Sb_4, with two magnetic sublattices having different values of magnetic moment, as predicted theoretically by Oleksy [12].

The physical properties of U_3Bi_4 have been the least investigated of the U_3X_4 pnictides, first, because of its extremely high pyrophoricity and second, because for a long time single crystals were not available. The recently grown single crystals enable some progress in studies of anisotropic properties of this compound. U_3Bi_4 orders magnetically below $T_c = 108$ K; its lattice parameter found by x-ray scattering [13] is equal to 9.368 Å. This

§ To whom correspondence should be addressed; e-mail: wisniew@highscreen.int.pan.wroc.pl

0953-8984/96/4910589+12$19.50

results in the distance between nearest U–U neighbours being equal to 4.375 Å, which is slightly bigger than that in U_3Sb_4 (4.255 Å) [13].

If the change of the easy magnetization axis direction in U_3Sb_4 is due to increase of the pnictogen anion radius [1], a collinear magnetic structure might be expected in U_3Bi_4 as well. Since no direct evidence of the existence of such a structure has been given so far, neutron scattering experiments have been performed on single crystals of U_3Bi_4 and U_3Sb_4 and results are presented here.

2. Crystal and magnetic structure

The unit cell of a U_3X_4-type compound contains 12 uranium cations and 16 pnictogen anions. After taking into account body centring of the elementary cell one can distinguish in the structure six equivalent sublattices (see table 1).

Table 1. The positions of uranium ions in the unit cell and their local $\bar{4}$-axes.

Ion	*x*	*y*	*z*	Local symmetry axis
U1	3/8	0	1/4	[100]
U2	1/8	0	3/4	[100]
U3	1/4	3/8	0	[010]
U4	3/4	1/8	0	[010]
U5	0	1/4	3/8	[001]
U6	0	3/4	1/8	[001]

Each cation has eight nearest anion neighbours, which form an octaverticon with the point symmetry D_{2d}. A $\bar{4}$-axis of each octaverticon is parallel to one of the main cubic axes of the crystal. The octaverticon can be divided into two tetrahedra: one elongated and another flattened along the $\bar{4}$-axis. An example of the arrangement of neighbouring pnictogen anions around an uranium cation is shown in figure 1.

The particularities of the symmetry of the U_3X_4 crystal structure were considered within the phenomenological spin model introduced and developed by Przystawa and Oleksy [11, 12]. This model takes into account an anisotropic exchange interaction, an interaction with external magnetic field and a locally anisotropic crystal field.

The Hamiltonian can be written as follows:

$$\mathcal{H} = -\frac{1}{2}\sum_{i,j}\sum_{gi,gj}\sum_{\alpha} J^{\alpha\alpha}_{gi,gj} S^{\alpha}_{gi} S^{\alpha}_{gj} - \sum_{i,gi,\alpha} H^{\alpha} S^{\alpha}_{gi} + \mathcal{H}_{CF} \qquad (1)$$

where S^{α}_{gi} is the αth component of the spin operator at the gth site in sublattice i ($i = 1, 2, ..., 6$), $\hat{J}_{gi,gj}$ is the anisotropic exchange-interaction tensor limited to the nearest neighbours and H^{α} is the αth component of the external magnetic field. The $\mathcal{H}_{CF}$ denotes the crystal field Hamiltonian.

The mean field analysis of the Hamiltonian (1) shows [11] that such a system can order magnetically, and that the most general types of magnetic structure allowed are the following:

(i) the *C* structure which is a non-collinear, three-sublattice magnetic structure with

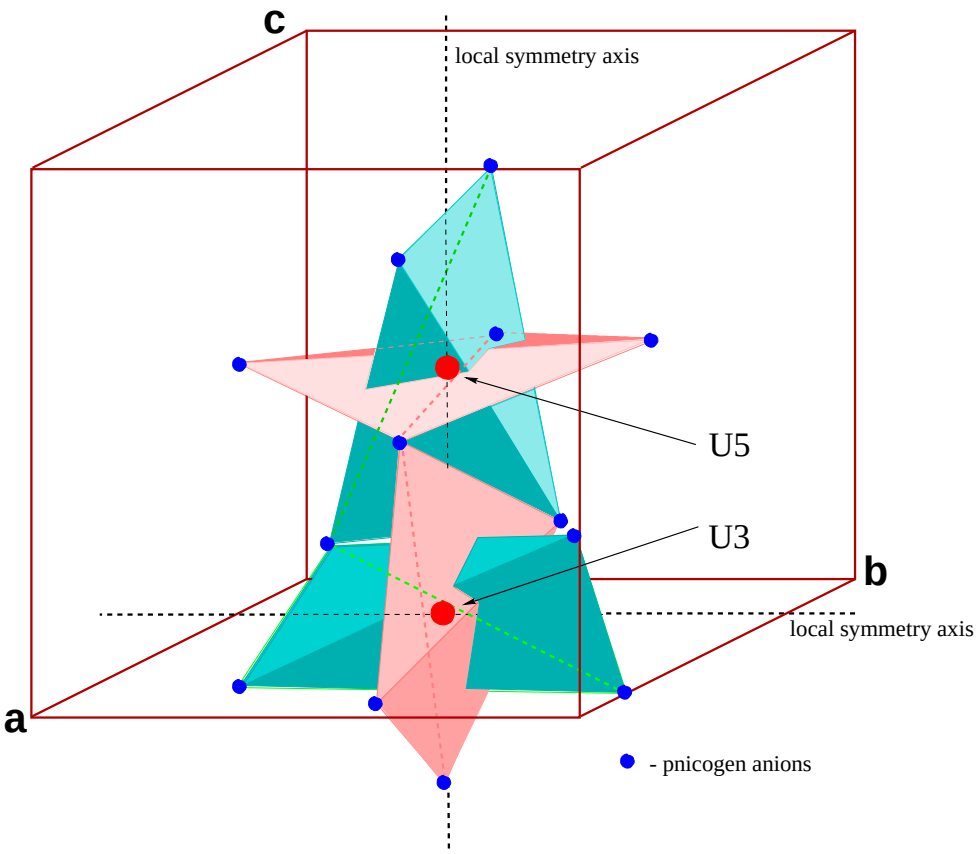

Figure 1. Arrangement of pnictogen anions in the neighbourhood of two uranium cations, U3 and U5, having mutually perpendicular local symmetry axes.

a ferromagnetic component along the [111] axis, as shown in figure 2

$$\mu_1 = \mu_{U1} = \mu_{U2} = \begin{pmatrix} v \\ w \\ w \end{pmatrix} \qquad \mu_2 = \mu_{U3} = \mu_{U4} = \begin{pmatrix} w \\ v \\ w \end{pmatrix}$$
$$\mu_3 = \mu_{U5} = \mu_{U6} = \begin{pmatrix} w \\ w \\ v \end{pmatrix}; \tag{2}$$

(ii) the *P* structure which is also a non-collinear, three-sublattice structure with the magnetic moments parallel to the (110) plane,

$$\mu_1 = \mu_{U1} = \mu_{U2} = \begin{pmatrix} v \\ u \\ 0 \end{pmatrix} \qquad \mu_2 = \mu_{U3} = \mu_{U4} = \begin{pmatrix} u \\ v \\ 0 \end{pmatrix}$$
$$\mu_3 = \mu_{U5} = \mu_{U6} = \begin{pmatrix} w \\ w \\ 0 \end{pmatrix}; \tag{3}$$

(iii) the L structure which is collinear and consists of two sublattices. All moments, as shown in figure 3, are parallel to the [001] axis.

$$\mu_1 = \mu_{U5} = \mu_{U6} = \begin{pmatrix} 0 \\ 0 \\ v \end{pmatrix} \qquad \mu_2 = \mu_{U1} = \mu_{U2} = \mu_{U3} = \mu_{U4} = \begin{pmatrix} 0 \\ 0 \\ w \end{pmatrix}. \tag{4}$$

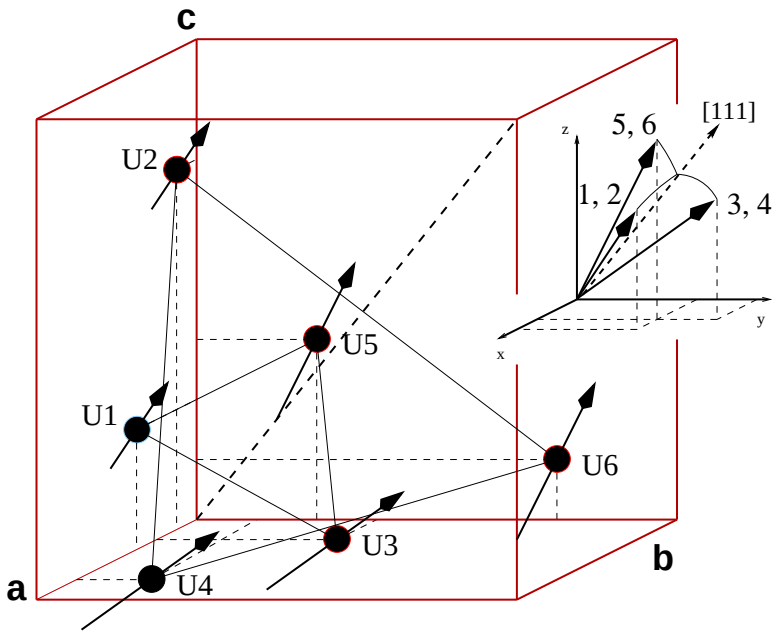

Figure 2. C-type non-collinear, three-sublattice magnetic structure with effective easy magnetic axis along the [111] crystal axis.

All three models of spin structure presented above are the same as obtained from the Landau thermodynamic potential in the 'exchange approximation' taking into account only the forces which can be written in the form of the scalar product of the spins. As shown by Oleksy [12] the 'relativistic forces' violating this condition may lead to appearance of additional spin non-collinearity. In this case the L-structure transforms into the non-collinear L':

$$\mu_{U1} = \begin{pmatrix} 0 \\ -\gamma \\ w \end{pmatrix} \qquad \mu_{U2} = \begin{pmatrix} 0 \\ \gamma \\ w \end{pmatrix} \qquad \mu_{U3} = \begin{pmatrix} \gamma \\ 0 \\ w \end{pmatrix}$$
$$\mu_{U4} = \begin{pmatrix} -\gamma \\ 0 \\ w \end{pmatrix} \qquad \mu_{U5} = \mu_{U6} = \begin{pmatrix} 0 \\ 0 \\ v \end{pmatrix}. \tag{5}$$

This non-collinearity can be characterized by an angle $\theta = \tan^{-1}(\gamma/w)$, between the [001] direction and the magnetic moments of atoms U1, U2, U3 and U4 and should be smaller compared to the non-collinearity of the three-sublattice C-structure which is due to 'exchange forces'. Recently Sandratskii and Kübler [14] have done first-principles calculations of the magnetic structure of U_3X_4 compounds (X = P, As, Sb), which revealed that for U_3Sb_4 the ground state magnetic structure is of the L' type.

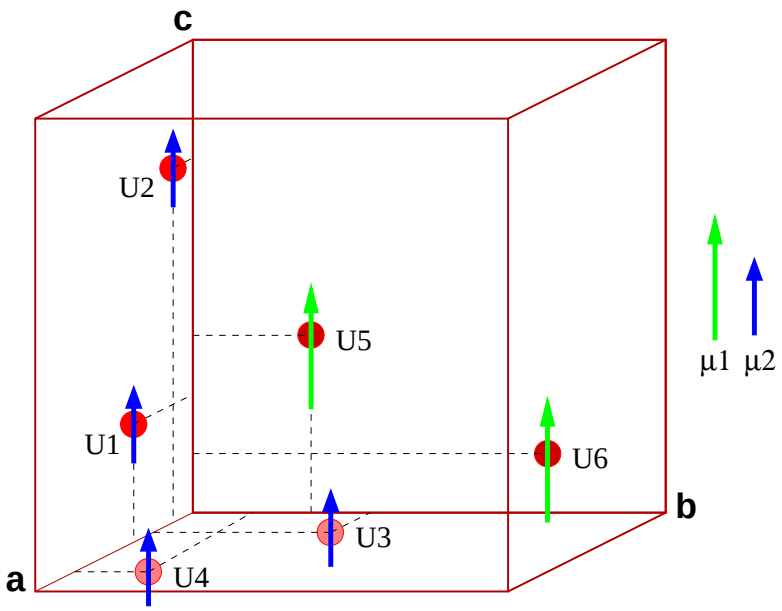

Figure 3. *L*-type collinear magnetic structure with two different types of U site having different values of magnetic moment and effective easy magnetic axis along the [001] crystal axis.

3. Experimental details

The U_3Bi_4 single crystals were grown using the molten metal solution evaporation method described in detail elsewhere [15]. ^{238}U of nuclear purity (3N chemical purity) and distilled bismuth (of 4N purity) were used as substrates. Slow evaporation of an excess of Bi at constant temperature was carried out in a graphite crucible sealed in a quartz ampoule with helium atmosphere and heated with an induction coil. A neutron diffraction study was performed on one of the crystals of dimensions $3 \times 3 \times 2$ mm^3. The U_3Sb_4 single crystals were grown by a modified van Arkel method described in [16]. A U_3Sb_4 single crystal of dimensions $3 \times 3 \times 3$ mm^3 was chosen for the neutron experiments. The crystals of both compounds were enclosed in aluminum containers with helium atmosphere containing less than 1 ppm of O_2 and H_2O to avoid oxidation.

Neutron diffraction studies were carried out at the ORPHÉE reactor, LLB, Saclay. Integrated intensities were collected on the four-circle diffractometer 6T2 using $\lambda = 1.5$ Å and $\lambda = 0.9$ Å in a Displex refrigerator. Pyrolitic graphite (at $\lambda = 1.5$ Å) and Er (at $\lambda = 0.9$ Å) filters were used to suppress higher-order contaminations. Polarized neutron flipping ratios were measured on the polarized neutron diffractometer 5C1 with wavelength $\lambda = 0.845$ Å, in magnetic field up to 5 T.

Refinements based on the measured structure amplitudes and flipping ratios were performed using programs MAGLSQ and POLSQ of the *Cambridge Crystallography Subroutine Library* [17]. The quality of refinement is characterized below by standard quantities:

$$R = \frac{\sum |G_{\mathrm{obs}} - G_{\mathrm{calc}}|}{\sum G_{\mathrm{obs}}} \qquad R_W = \frac{\sum w\,|G_{\mathrm{obs}} - G_{\mathrm{calc}}|}{\sum w\,G_{\mathrm{obs}}}$$

$$\mathrm{GooF} = \sqrt{\frac{\sum w^2 (G_{\mathrm{obs}} - G_{\mathrm{calc}})^2}{N_{\mathrm{obs}} - N_{\mathrm{var}}}} \qquad w = 1/\sigma^2 \tag{6}$$

where G_{obs} and G_{calc} are observed and calculated structure factors or flipping ratios, σ is an experimental error (of G_{obs}). N_{obs} and N_{var} denote numbers of observations and refined variables, respectively.

In the refinement the theoretical form factor of the U^{4+} ion was used in an analytical approximation to the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ given in [18].

4. Results

4.1. Unpolarized neutron study of U_3Sb_4

Prior to the low-temperature study the crystal was characterized using the four-circle neutron diffractometer at room temperature: 986 reflections were measured with the wavelength $\lambda = 0.9$ Å and 448 reflections with $\lambda = 1.5$ Å. The former collection was used to refine the single adjustable positional parameter, x of Sb, occupation factors and the isotropic temperature factors, see table 2, and the latter mainly to determine the extinction parameters, which were found to be insignificant in the refinement. The refinement shows that the crystal is perfectly stoichiometric and its structure parameters agree well with these obtained earlier in the x-ray experiments (see table 2).

Table 2. The results of refinement on structure factors measured for U_3Sb_4 at 300 K. In this and the following tables anisotropic temperature factors are described by $\exp(-2\pi^2(u_{11}h^2a^{*2} + \cdots + u_{23}kb^*lc^* + \cdots))$.

Total measured reflections	986
Independent reflections	260
λ	0.9 Å
$\sin\theta/\lambda$	<0.95 Å^{-1}
Sb x, y, z	0.079 28(11)
Sb $u_{11} = u_{22} = u_{33}$	0.0111(3)
Sb $u_{12} = u_{23} = u_{13}$	0.0006(3)
U $u_{11} = u_{22}$	0.0107(3)
U u_{33}	0.0100(5)
R	7.84%
R_W	4.66%
GooF	2.40

Further measurements were carried out at 10 K using two wavelengths as well. The refinement was carried out for both wavelengths simultaneously, see table 3, since a test of separate refinement gave very close results for all crystal and magnetic parameters. As a first step, a model of simple ferromagnet was refined ($\mu_1 = \mu_2$), which describes the measured structure factors quite well (see table 3) and gives the value of U magnetic moment equal to 1.71(5) μ_B. This can be done using the $I\bar{4}3d$ space group. To refine the L-type magnetic structure, however, one need to use a group of lower symmetry (tetragonal or orthorhombic) allowing the presence of different magnetic moments on the different U sites. As a consequence new atomic positional parameters may appear due to lower symmetry of the crystal after the phase transition. Different subgroups of $I\bar{4}3d$ were tested in order to find possible structural distortions. In all cases the magnetic and structural

parameters were refined simultaneously, supposing the presence of perfect pseudo-cubic twinning. Since no evidence was found for the presence of structural distortion, further refinements were limited using the tetragonal space group ($I\bar{4}2d$) and assuming a perfect pseudo-cubic twinning. In this case the magnetic moments μ_1 and μ_2 can be refined separately. As seen from table 3, if the constraint on μ_1 and μ_2 is removed the fit of results improves slightly and shows a considerable difference in the magnitude of magnetic moments μ_1 and μ_2. At first sight the changes of R-factor look rather small, but one should take into account that the total magnetic contribution in the scattering is relatively small as the data include a large number of purely nuclear reflections and the magnetic ones at high scattering angles have low magnetic form-factor values. If the refinement were performed on a set of reflections limited to small scattering angles the improvement of the R-factor would be more pronounced.

Table 3. The results of refinement on structure factors measured for U_3Sb_4 at 10 K; the value of 2.14 μ_B for fixed μ_1 was taken from polarized neutron data refinement.

	Constraint		
	$\mu_1 = \mu_2$	None[a]	$\mu_1 = 2.14\ \mu_B$
Total measured reflections:	712 with $\lambda = 0.9$ Å, $\sin\theta/\lambda < 0.95$ Å^{-1}		
	377 with $\lambda = 1.5$ Å, $\sin\theta/\lambda < 0.54$ Å^{-1}		
Sb x, y, z	0.0798(1)	0.0798(1)	0.0798(1)
Sb u_{ii}	0.0028	0.0028	0.0031
U u_{ii}	0.0025	0.0025	0.0026
μ_1 (μ_B)	1.71(5)	2.34(5)	2.14 (fixed)
μ_2 (μ_B)	1.71(5)	1.38(5)	1.47(5)
R (%)	6.48	6.10	6.19
R_W (%)	4.32	3.94	4.02
GooF	3.81	3.38	3.46

[a] Correlation between μ_1 and μ_2 was −91%.

4.2. Polarized neutron study of U_3Sb_4

Since polarized neutron experiments are considerably more sensitive to small changes of magnetic structure, polarized neutron flipping ratios were measured for three different values of applied field: 1.5, 2.0 and 3.0 T at 8 K. In this range of magnetic field we did not observe any dependence of the flipping ratios on the field value. The most extensive set of data was collected with the field of 3.0 T applied. The crystal was mounted with the [001] axis parallel to the field direction. A total of 194 flipping ratios were measured up to $\sin\theta/\lambda = 0.85$ Å^{-1}. Since the crystal structure of U_3Sb_4 is non-centrosymmetric, neither calculation of the magnetic structure factors from the measured flipping ratios (R_F) nor the averaging of symmetry equivalent hkl was performed. The measured R_F values were used directly in the refinement by the POLSQ program. This program allows extinction to be taken into account, but as no significant extinction parameters were obtained from the integrated intensity measurements, extinction corrections were not performed. The polarization of the incident neutron beam has been determined by measuring the flipping ratio of the (2 0 0) reflection from a Co(Fe) single crystal in the sample position and was found to be $P_0 = 0.92$. It is worth noting that when the incident polarization was allowed to vary, slightly better consistency of the data was achieved at $P_0 = 0.895$, which indicated the presence of some

depolarization in the crystal probably due to a small misalignment of the easy magnetic axis and the applied field. Since the changes of the model parameters resulting from the variation of the incident polarization remained within the experimental errors and such a variation was not sufficiently justified, only the results obtained using $P_0 = 0.92$ are given below.

The results of refinements on flipping ratios performed using the model of a simple magnetized ferromagnet and the *L*-model with different magnetic moments of U at different sites are shown in table 4. As seen from the table the former model already gives a satisfactory description of the data with the average U magnetic moment 1.82(4) μ_B in a reasonable agreement with the results of the unpolarized neutron study (1.71(5) μ_B), however the value of the moment determined by magnetization measurements is higher and amounts to 2.00 μ_B at 4.2 K [11]. Considerable improvement of the refinement is achieved when the constraint on the values of U moments is removed, giving quite a big difference in the values of the moments μ_1 and μ_2 ($\mu_1 = 2.14(6)$ μ_B, $\mu_2 = 1.66(5)$ μ_B; the difference is about 26% of the average moment).

Table 4. The results of refinement on 194 flipping ratios measured for U_3Sb_4.

	Constraint	
	$\mu_1 = \mu_2$	None
λ	0.845 Å	
$\sin\theta/\lambda$	<0.85 Å^{-1}	
μ_1 (μ_B)	1.82(4)	2.14(6)
μ_2 (μ_B)	1.82(4)	1.66(5)
R_W (%)	7.92	6.35
GooF	1.62	1.33

Thus the polarized neutron experiment confirms the results obtained from the integrated intensity measurements, proving the presence of the *L*-type ordering in U_3Sb_4. (A table of the observed and calculated values of flipping ratios that illustrates the quality of the final refinement can be obtained from the authors on request.)

It should be noted that the form factor of U used in the refinement was described by radial integrals $\langle j_0 \rangle$ and $\langle j_2 \rangle$ given in [18] for the U^{4+} ion and our attempt to refine the spin and orbital components of the moment separately was unsuccessful because of strong correlation of these parameters in the refinement.

Finally, as mentioned above, we tried to find evidence for the 'relativistic non-collinearity' by introducing the angle $\theta = \tan^{-1}(\gamma/w)$ described above. The result of the refinement has shown that the best fit of the flipping ratios is achieved with $\theta = 3.7(3.3)^\circ$, which shows that the 'relativistic effects' are beyond our experimental possibilities. It is worth noting that Sandratskii and Kübler in their recent calculations [14] have found for U_3Sb_4 rather small value of non-collinearity angle, $\theta = 7.0$ degrees.

4.3. Unpolarized neutron study of U_3Bi_4

A single crystal of U_3Bi_4 was characterized on the four-circle neutron diffractometer with wavelength $\lambda = 0.9$ Å. A total of 377 reflections have been measured at room temperature. The results of refinement on the measured structure factors presented in table 5 confirm 3:4 stoichiometry. The only adjustable structural parameter, x of Bi, agrees with that

previously obtained by x-ray measurements [13] and the isotropic temperature factors are close to those of U_3Sb_4. The mosaicity of the crystal was about 20 minutes of arc and the extinction corrections did not improve the quality of refinement.

Table 5. The results of refinement on structure factors collected on U_3Bi_4 at 300 K.

Total measured reflections	377
Independent reflections	136
λ	0.9 Å
$\sin\theta/\lambda$	$<$0.95 Å^{-1}
Bi x, y, z	0.078 39(14)
Bi $u_{11} = u_{22} = u_{33}$	0.0079(4)
Bi $u_{12} = u_{23} = u_{13}$	0.0004(5)
U $u_{11} = u_{22}$	0.0093(7)
U u_{33}	0.0087(10)
R	9.00%
R_W	4.34%
GooF	1.82

Further measurements were carried out at 10 K. A total of 333 reflections were measured, up to $\sin\theta/\lambda = 0.96$ Å^{-1}. A rather strong magnetic contribution to the reflections of the U sublattice was detected indicating that the main component of the U moment is ordered ferromagnetically. Refinement of the model of a simple ferromagnet with an equal domain population gives the average value of U moment 1.76(5) μ_B and a reasonable agreement factor (table 6). Refinement of the L-model, similar to that of U_3Sb_4, gives slightly better agreement and indicates the difference of the magnetic moments of U of the order of 30% on the two types of U sites, see table 6. From a quantitative point of view, however, this result could be probably contested. First, since the net magnetization of U_3Bi_4 is unknown other models should be considered. Second, the result of refinement depends strongly on the precision of the integrated intensity measurements of small peaks which might be influenced by multiple scattering. In order to clarify this uncertainty polarized neutron measurements were performed.

4.4. Polarized neutron study of U_3Bi_4

The first aim of this study was to determine the easy magnetization axis of U_3Bi_4. A total of 188 polarized neutron flipping ratios were measured at wavelength $\lambda = 0.845$ Å in the field of 3.0 T at 8 K. Non-averaged flipping ratios were used in the refinement. It happened that when the sample was mounted in the superconducting magnet its crystal symmetry axis [001] was only 27 degrees away from the applied field direction. Since the crystal was encapsulated in Al container and its orientation was not easy to handle, we performed measurements keeping this orientation. This misalignment appeared to be not particularly important as the mutual orientation of the field and the easy magnetization axis is taken into account in the POLSQ program.

First, refinement on flipping ratios was performed for the model of a simple ferromagnet with magnetic moments locked along the [001] axis closest to the applied magnetic field. The value of U magnetic moment obtained from the refinement is 1.88(5) μ_B (table 7), being close to the value of 1.76(5) μ_B determined from unpolarized neutron data. Afterwards the other possible orientations of the easy magnetization axis were tested ([011] and [111]).

Table 6. The results of refinement on structure factors collected on U_3Bi_4 at 10 K; the value of 2.11 μ_B for fixed μ_1 was taken from polarized neutron data refinement.

	Constraint		
	$\mu_1 = \mu_2$	None[a]	$\mu_1 = 2.11\ \mu_B$
Total measured reflections		333	
λ		0.9 Å	
$\sin\theta/\lambda$		<0.96 Å^{-1}	
Bi x, y, z	0.0786(1)	0.0787(1)	0.0787(1)
Bi u_{ii}	0.0041	0.0047	0.0049
U u_{ii}	0.0033	0.0036	0.0039
μ_1 (μ_B)	1.76(5)	2.07(5)	2.11 (fixed)
μ_2 (μ_B)	1.76(5)	1.50(5)	1.44(5)
R (%)	6.94	6.36	6.27
R_W (%)	4.71	4.29	4.22
GooF	2.41	2.16	2.13

[a] Correlation between μ_1 and μ_2 was −95%.

Neither of the latter models gave a satisfactory description of the data, which suggested that the easy magnetization axis of U_3Bi_4 is the same as that of U_3Sb_4, namely the [001] axis.

Second, the values of moments belonging to different U sites were varied independently, which corresponds to the model of the *L*-type collinear structure. As seen from table 7 this model gives a considerably better agreement factor than the simple ferromagnet model. As in the case of U_3Sb_4 the resulting magnetic moments of U at different sites are different: μ_1=2.11(5) μ_B and μ_2=1.81(4) μ_B. The difference is about 16% of the average moment, which indicates the high magnetic anisotropy of U_3Bi_4 and confirms the presence of the *L*-type ordering in this compound.

Table 7. The results of refinement on 188 flipping ratios measured for U_3Bi_4. Easy magnetization axis, [001].

	Constraint	
	$\mu_1 = \mu_2$	None
λ	0.845 Å	
$\sin\theta/\lambda$	<0.72 Å^{-1}	
μ_1 (μ_B)	1.88(5)	2.11(5)
μ_2 (μ_B)	1.88(5)	1.81(4)
R_W (%)	8.49	7.33
GooF	1.45	1.21

5. Discussion

Polarized and unpolarized neutron scattering results confirm that, for both U_3Sb_4 and U_3Bi_4, the magnetic structure is collinear, with two magnetic sublattices, as described by Oleksy [12] and proposed in [11]. The values of magnetic moment for these two sublattices are 2.14 and 1.66 μ_B for the antimonide, and 2.11 and 1.81 μ_B for the bismuthide.

The difference between the magnetic moments on different uranium sites is due to a

low local symmetry of the U environment. A decrease in this difference from 26% to 16% observed when the U nearest-neighbour distance increases from 4.255 Å for U_3Sb_4 to 4.375 Å for U_3Bi_4 supports earlier suggestions [19, 20, 1] that hybridization plays a significant role in the appearance of magnetic anisotropy in U_3X_4-type pnictides.

The average values of U magnetic moment, 1.82 μ_B and 1.88 μ_B obtained from the neutron scattering data for U_3Sb_4 and U_3Bi_4, respectively, are higher than similar values in the other two compounds of this series, U_3P_4 (1.39 μ_B) and U_3As_4 (1.65 μ_B). They remain, however, considerably smaller than the free ion value 3.2(5) μ_B for the U^{4+} ion. A strong reduction of the magnetic moment compared to the free ion value may be due to crystal field effects and 5f electron delocalization. Since the hybridization weakens with increasing pnictogen radius, p states shift down in energy and their overlap with the conduction band (directly observed via the carrier concentration: 0.026, 0.014 and 0.0079 per U ion for U_3P_4, U_3As_4 and U_3Sb_4, respectively) decreases. This leads to stronger localization of the f states and results in a progressive increase in the average magnetic moment per uranium ion, which changes from 1.39 μ_B for U_3P_4 to 1.88 μ_B for U_3Bi_4.

The value of the average magnetic moment for U_3Sb_4 agrees reasonably well with the value estimated from magnetization measurements (2.00(1) μ_B [11]). The discrepancy of about 10% can be explained by the fact that the spherical approximation for the magnetic form factor used in the refinement did not allow us to refine the ratio of the spin and orbital components of the moment. Further analysis of the space distribution of moment density and refinement of a non-spherical model, which can clarify this problem, are in progress.

Finally, we would like to note that the refinement of polarized neutron data allowed us to determine the direction of the easy magnetization axis in U_3Bi_4, which appeared to be [001], as in U_3Sb_4.

Acknowledgments

This work was partially supported by Polish Committee for Scientific Research, grant No KBN-2 P302 173 06. Part of the neutron scattering experiments was supported via the Human Capital and Mobility—Access to Large Scale Facilities PECO Extension (contract ERB CIPD CT 940080). The stay of P Wiśniewski at LLB was financed by the French Ministry of Education and Scientific Research as a part of the Network programme.

Special thanks are due to P J Brown for her help and advice in installation of the *Cambridge Crystallography Subroutine Library* and associated refinement programs in Saclay.

References

[1] Maślanka R, Henkie Z, Franse J J M, Verhoef R, Oleksy Cz and Przystawa J 1989 *Physica* B **159** 181
[2] Crabtree G W 1985 *J. Magn. Magn. Mater.* **52** 169
[3] Fournier J M and Troć R 1985 *Handbook on the Physics and Chemistry of Actinides* vol 2, ed A J Freeman and G H Lander (Amsterdam: North-Holland) p 61
[4] Schoenes J S, Küng M, Hauert R and Henkie Z 1983 *Solid State Commun.* **47** 23
[5] Henkie Z, Johanson W R, Arko A J, Crabtree G W and Bazan C 1983 *Phys. Rev.* B **28** 4198
[6] Inada Y, Aono H, Takeda N, Sato N, Sawada A, Suzuki M, Suzuki T and Komatsubara T 1993 *Physica* B **186–188** 761
[7] Inada Y, Aono H, Kimura J, Ishiguro A, Sato N, Sawada A, Komatsubara T, Kaczorowski D and Troć R 1994 *Physica* B **194–196** 1173
[8] Burlet P, Rossat-Mignod J, Troć R and Henkie Z 1981 *Solid State Commun.* **39** 745
[9] Buhrer C F 1969 *J. Phys. Chem. Solids* **30** 1273
[10] Przystawa J 1970 *J. Phys. Chem. Solids* **31** 2158

[11] Henkie Z, Maślanka R, Oleksy Cz, Przystawa J, de Boer F R and Franse J J M 1987 *J. Magn. Magn. Mater.* **68** 54
[12] Oleksy Cz 1984 *Acta Phys. Polon.* A **66** 665
[13] Troć R, Mulak J and Suski W 1971 *Phys. Status Solidi* b **43** 147
[14] Sandratskii L M and Kübler J 1995 *Phys. Rev. Lett.* **75** 946; 1996 *Physica* B **217** 167; private communication
[15] Henkie Z, Wiśniewski P and Gukasov A 1996 *J. Cryst. Growth* accepted for publication
[16] Henkie Z and Markowski P J 1977 *J. Cryst. Growth* **41** 303
[17] Brown P J and Matthewman J C 1993 *Cambridge Crystallography Subroutine Library* Mark 3, Rutherford Appleton Laboratory, 93-009
[18] Brown P J 1992 *International Tables for Crystallography* vol C, ed A J C Wilson (Dordrecht: Kluwer) p 391
[19] Tagekahara K, Yanase A and Kasuya T 1982 *Crystalline Electric Fields and f-electron Magnetism* ed R P Guertin, W Suski and Z Żołnierek (New York: Plenum) p 533
[20] Suzuki T, Takagi S, Niitsuma N, Tagekahara K, Kasuya T, Yanase A, Sakakibara T, Date M, Markowski P J and Henkie Z 1983 *High Field Magnetism* ed M Date (Amsterdam: North-Holland) p 183