PHYSICAL REVIEW B VOLUME 60, NUMBER 9 1 SEPTEMBER 1999-I

Spin and orbital moments in U_3X_4-type pnictides (X=P, As, Sb, Bi): Polarized neutron-diffraction study

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(Received 12 February 1999; revised manuscript received 26 April 1999)

Polarized neutron experiments have been performed on single crystals of U_3P_4, U_3As_4, U_3Sb_4, and U_3Bi_4. The spin and orbital components of the magnetic moments on the uranium atoms were separated within the dipole magnetic form factor approximation and compared to the theoretical values. The ratio of these components indicates an important hybridization of $5f$-electron states with the conduction band for all four compounds. The hybridization estimated in this way differs significantly for two uranium sublattices in U_3Sb_4. [S0163-1829(99)01533-7]

All four pnictides of U_3X_4-series crystallize in the body-centered-cubic structure (T_d^6 or $I\bar{4}3d$ space group.) They order magnetically below fairly high Curie temperatures (108–198 K) and their U-$5f$ electrons hybridize with conduction band electrons.[1–6] As the hybridization weakens with increasing nearest uranium neighbors distance $d_{\text{U-U}}$ the carrier concentration decreases from 0.026 to 0.014 and to 0.0079 per U ion for U_3P_4, U_3As_4, and U_3Sb_4, respectively,[1] which is due to a decrease in the overlap of p-states with the conduction band. The unit cell of U_3X_4-type compounds contains 12 uranium cations and 16 pnictogen anions. After taking into account body-centering of the unit cell, one can distinguish in the structure six equivalent sublattices of uranium ions. Details of the crystal and magnetic structures were described in Refs. 7,8.

An interesting feature of this structure is the fact that despite the overall cubic symmetry, the local symmetry of the U-ion neighborhood is tetragonal. In consequence, the uranium sublattice can be divided into three sublattices, with the $\bar{4}$-symmetry axes parallel to one of three main cubic axes. Further we denote the magnetic moments of U ions in these three sublattices as μ_1,μ_2, and μ_3, respectively. Such low local symmetry leads to remarkable anisotropic magnetic and electron transport properties (for a review see Ref. 9.)

The theoretical symmetry analysis of the crystal structure by Przystawa and Oleksy predicted possible magnetic phases in the U_3X_4 series.[10–12] The C phase, a noncollinear, three-sublattice magnetic structure with a ferromagnetic component along the [111] direction: $\mu_1=(v,w,w),\mu_2=(w,v,w),\mu_3=(w,w,v)$ in which moments are tilted from [111] towards cubic axes by certain angle ϑ, was postulated for U_3P_4 and U_3As_4. The L phase, a collinear structure consisting of two sublattices $\mu_1=\mu_2=(0,0,v),\mu_3=(0,0,w)$, with all moments parallel to [001], was proposed for U_3Sb_4 and U_3Bi_4.

The first U_3X_4 pnictides to be studied by means of neutron scattering on single crystals were U_3P_4 and U_3As_4.[13] The magnetic structure corresponding to the C phase was found for both compounds. Values of 25(5)° and 13(6)° for ϑ and $1.89(0.3)\mu_B$ and $1.42(0.2)\mu_B$ for the magnetic moments were found in U_3As_4 and U_3P_4, respectively.

Recently our polarized and unpolarized neutron scattering results confirmed that U_3Sb_4 and U_3Bi_4 are both in the L phase at zero external field.[8] At the same time qualitatively similar theoretical results were shown by Sandratskii and Kübler.[14,15] Their electron band calculations yielded the same types of structure, but the value of ϑ calculated for U_3P_4 was 1.5°. The big discrepancy between theoretical values of ϑ and the values determined experimentally,[13] induced us to remeasure this angle for U_3As_4 and U_3P_4 prior to the spin and orbital moment measurements.

The U_3P_4 and U_3As_4 single crystals have been grown by conventional chemical transport method. The U_3Sb_4 and U_3Bi_4 single crystals have been grown by a modified van Arkel method,[16] and a molten metal solution evaporation method,[17] respectively. The ^{238}U of nuclear purity ($3N$ chemical purity) and distilled pnictogens (of 4N purity) were used in all syntheses. A neutron diffraction study of all four compounds was carried out on the single crystals of approximate dimensions of $3\times3\times2$ mm^3.

Perfoming measurements on the four-circle diffractometer *6T2* at L.L.B.-Saclay (neutron wavelength of 0.9 and 1.5 Å), we noted that some reflections forbidden by the $I\bar{4}3d$ group symmetry had nonzero intensity even at room temperature, when the sample was in the paramagnetic state. Moreover, the intensities of symmetrically equivalent forbidden reflections were significantly different. This indicated that this effect could be due to the multiple scattering.

The multiple scattering occurs when two or more, sets of crystal planes simultaneously satisfy Bragg's condition. This effect can be particularly severe in the case of large unit cells, as those of uranium pnictides. One of the consequences of multiple scattering is the appearance of peaks at ''forbidden'' reflection positions. On the other hand, the noncollinear C-type magnetic structure is also characterized by the presence of purely magnetic reflections of (110)- and (002)-type at the forbidden positions. The intensities of these reflections are proportional to $\sin^2\vartheta$ and were reported to be

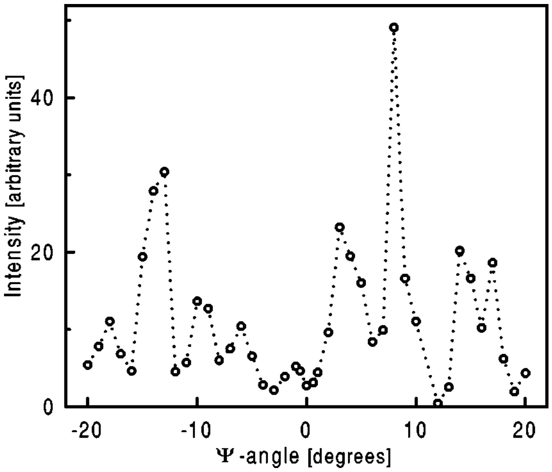

FIG. 1. Angular dependence of integrated intensity for (0 0 2) reflection measured for U_3As_4 at room temperature. Ψ denotes the angle by which the sample was rotated around the scattering vector.

about two orders of magnitude smaller than those of strongest nuclear reflections.[13] Since the precision of measurement of these reflections is vital in the determination of ϑ, we became convinced that no reliable information about the noncollinearity angle can be obtained without a thorough analysis of multiple scattering.

It is known that the condition of multiple scattering can be changed by rotation of the crystal around the scattering vector. This can be realized by a so called Renninger scan (or Ψ scan) which can be easily performed on the four-cirle diffractometer. One of such scans of (0 0 2) reflection measured at room temperature on U_3As_4 is shown in Fig. 1. As seen from this figure the intensity of forbidden reflection practically never vanishes except for the very narrow angular regions of Ψ.

In order to suppress the multiple scattering Ψ scans were performed at room temperature and the Ψ angular regions not contaminated by multiple scattering were determined for all equivalent reflections of the (1 1 0) and (2 0 0) type. These regions were chosen for subsequent measurements of integrated intensity at room temperature and at 15 K. The difference of integrated intensities measured at 15 and 300 K obtained in such a way was considered as magnetic intensity and used to refine the values of noncollinearity angles. For U_3P_4 no magnetic contribution was found in any of equivalent reflections of both types within experimental accuracy. Very small but evident magnetic contribution was found in the (1 1 0)- and (2 0 0)-type reflections in U_3As_4. We should stress, however, that the intensities of these reflections were about one hundred times smaller than those reported in Ref. 13.

The magnetic intensities measured in such a way were used in the refinement performed with the MAGLSQ program of the Cambridge Crystallography Subroutine Library.[18] Obtained values of ϑ are one order of magnitude smaller than these from Ref. 13 and are shown, along with the most recent theoretical values obtained by Sandratskii and Kübler,[19] in Table I.

Spin and orbital moment measurements were performed using polarized neutron flipping ratio technique. The experiment was carried out on the 5C1 diffractometer with the wavelength $\lambda = 0.845$ Å, in the magnetic field up to 5 T and at the temperature of 4.2 K. An erbium filter was used to suppress higher order contaminations to less than 0.01%. Polarization of the incident neutron beam has been determined by measuring the flipping ratio of the (200) reflection from a Co(Fe) single crystal in the sample position and was found to be 0.91.

Since the crystal structure of U_3X_4 pnictides is noncentrosymmetric, neither calculation of the magnetic structure factors from the measured flipping ratios (R_F), nor the averaging on symmetry equivalent reflections was performed. The measured R_F values were used directly in the refinement by the POLSQ program of the Cambridge Crystallography Subroutine Library.[18] An extinction correction, using the Becker and Coppens Lorentzian model,[20] was applied in a

TABLE I. Magnetic structures in U_3X_4-type pnictides. Values of the noncollinearity angle ϑ are compared to previously reported experimental (Ref. 13) and theoretical (Ref. 19) ones.

	U_3P_4	U_3As_4	U_3Sb_4		U_3Bi_4	
	$\mu_{1,2,3}$	$\mu_{1,2,3}$	$\mu_{1,2}$	μ_3	$\mu_{1,2}$	μ_3
a [Å]	8.214	8.521	9.112		9.368	
$d_{\text{U-U}}$ [Å]	3.83	3.97	4.25		4.37	
easy axis	⟨111⟩	⟨111⟩	⟨001⟩		⟨001⟩	
measured R_F	254	155	194		188	
$\mu_L+\mu_S$ [μ_B]	1.34(6)	1.82(6)	1.72(4)	2.36(7)	1.96(4)	2.31(6)
μ_L [μ_B]	2.40(13)	3.15(9)	3.17(10)	3.64(14)	3.25(16)	3.63(24)
C_2	1.79	1.73	1.84	1.54	1.66	1.57
R_W [%]	4.10	3.72	6.16		7.00	
χ^2	0.99	0.84	1.30		1.37	
ϑ [deg.]	0.0(2.3) 13(6) [a]	3.1(0.5) 25(5) [a]	0		0	
ϑ_{theor} [deg.]	2.13 [b]	1.91 [b]	7.03 [b]			

[a] From Ref. 13.

[b] From Ref. 19.

TABLE II. Experimental and theoretical (Refs. 19,23) values of spin and orbital components of uranium magnetic moment in U_3X_4-type pnictides. All moment values are given in μ_B.

		μ_S		μ_L		$\mu_S+\mu_L$		$-\mu_L/\mu_S$	
formula	moment	expt.	theor.	expt.	theor.	expt.	theor.	expt.	theor.
U_3P_4	μ_1,μ_2,μ_3	$-1.06(14)$	-1.73	2.40	3.10	1.34	1.37	2.27(20)	1.79
U_3As_4	μ_1,μ_2,μ_3	$-1.33(10)$	-1.82	3.15	3.53	1.82	1.71	2.37(15)	1.94
U_3Sb_4	μ_1,μ_2	$-1.45(11)$	-1.90	3.17	3.94	1.72	2.04	2.19(14)	2.07
	μ_3	$-1.28(15)$	-1.99	3.64	4.18	2.36	2.19	2.85(20)	2.10
	per U ion					1.93	2.09	2.41	2.08
U_3Bi_4	μ_1,μ_2	$-1.29(17)$	-2.16	3.25	4.37	1.96	2.21	2.51(25)	2.02
	μ_3	$-1.32(25)$	-2.20	3.63	4.50	2.31	2.30	2.75(35)	2.05
	per U ion					2.08	2.24	2.59	2.03

case of U_3P_4 ($y_{\min}=0.6$) and U_3As_4 ($y_{\min}=0.92$). The parameters for this correction were obtained from the integrated intensity measurements. In a case of U_3Sb_4 and U_3Bi_4 no significant extinction was detected, hence the extinction correction was not applied.

The mutual orientation of the field and the easy magnetization axis is taken into account in the POLSQ program. Since the noncollinearity angles are very small or equal to zero, the refinement on flipping ratios was performed for collinear models in the case of all four compounds.

The magnetic amplitude of elastic neutron scattering on a particular magnetic ion with the moment μ and for the reflection corresponding to the scattering vector **Q** can be written as

$$\mu f(Q)=(\mu_S+\mu_L)f(Q). \tag{1}$$

$f(Q)$ denotes the magnetic form factor of this magnetic ion, μ_S a spin component and μ_L the orbital component of its total magnetic moment μ.

The magnetic form factor for $5f$ ions can usually be used in the dipole approximation[21]

$$f(Q)=\langle j_0(Q)\rangle+C_2\langle j_2(Q)\rangle,$$

where

$$C_2=\mu_L/(\mu_S+\mu_L). \tag{2}$$

Fitting of flipping ratios to those calculated from the magnetic amplitudes allowed us to separate spin and orbital components of the magnetic moments for each sublattice of uranium ions. In the refinement the theoretical form factor of U^{4+} ion was used as an analytical approximation to the $\langle j_0\rangle$ and $\langle j_2\rangle$ (Ref. 22) (the choice of another theoretical form factor, for instance that of U^{3+} is irrelevant in the refinement procedure, as will be discussed below.) The results of such refinement on the flipping ratios measured for U_3X_4 pnictides are collected in Table I. In Table II experimental values of the spin and orbital components are compared to those calculated by Sandratskii, Knöpfle, and Kübler.[19,23]

It is known that the refinement using radial integrals $\langle j_0\rangle$ and $\langle j_2\rangle$ for different ions (U^{3+}, U^{4+}, and U^{5+}) does not allow the determination of the ionization state of uranium because these integrals are very similar for all above ions.[21] On the other hand the $-\mu_L/\mu_S$ ratio depends strongly on the degree of hybridization,[24] the smaller the ratio, the stronger the hybridization.

As seen from Table II, the $-\mu_L/\mu_S$ values obtained for all compounds are very close to 2.5. At first sight this value corresponds well to the ratio 2.56 yield by the intermediate coupling scheme for the U^{3+}-free ion. The corresponding ratio for the U^{4+}-free ion is equal to 3.32. It should be noted, however, that the value 2.56 for U^{3+} ion was obtained without taking into account the hybridization of f electrons. On the other hand, strong experimental evidence for significant hybridization in U_3X_4 pnictides exists. Both optical spectroscopy and de Haas–van Alphen measurements indicate the hybridization.[3–6] For example U_3P_4 and U_3As_4 show rather large cyclotron effective masses of $22.9m_0$ and $14.8m_0$, respectively.[5,6] It is clear that if such a hybridization exists it should bring the $-\mu_L/\mu_S$ value for the U^{3+} ion well below 2.5 observed in experiment.

Moreover, the polarized neutron scattering provides not just the ratio $-\mu_L/\mu_S$, but the spin and orbital moments separately as well. One can see that the values of spin and orbital moments in all four compounds (Table II) are considerably reduced with respect to the free U^{4+} ion values $\mu_L=4.716\mu_B$ and $\mu_S=-1.432\mu_B$. This difference will be even more pronounced if we compare the experimental values of the magnetic moments with those of the U^{3+} ion, $\mu_L=5.585\mu_B$, $\mu_S=-2.169\mu_B$. Thus, in spite of a good agreement of the $-\mu_L/\mu_S$ ratio with that of the U^{3+} ion, we suggest that the ionic state of uranium in U_3X_4 pnictides is rather closer to a significantly hybridized $5f^2$ state than to the $5f^3$ one, bearing in mind of course, that the attribution of an ionic state to a semimetallic compound is a very crude approximation.

In conclusion we shall compare the results obtained here with those predicted by the LSDF theory (see Table II). The change of values of the average magnetic moment per uranium ion from one compound to another: $1.34\mu_B$ for U_3P_4, $1.82\mu_B$ for U_3As_4, $1.93\mu_B$ for U_3Sb_4, and $2.08\mu_B$ for U_3Bi_4 clearly reflects an evolution of hybridization with increasing nearest uranium neighbor distance $d_{\text{U-U}}$ (the free ion values are $3.416\mu_B$ and $3.284\mu_B$ for U^{3+} and U^{4+}, respectively.) The LSDF theory overestimates both spin and orbital components of the moments but predicts rather well the total resulting moment of uranium.

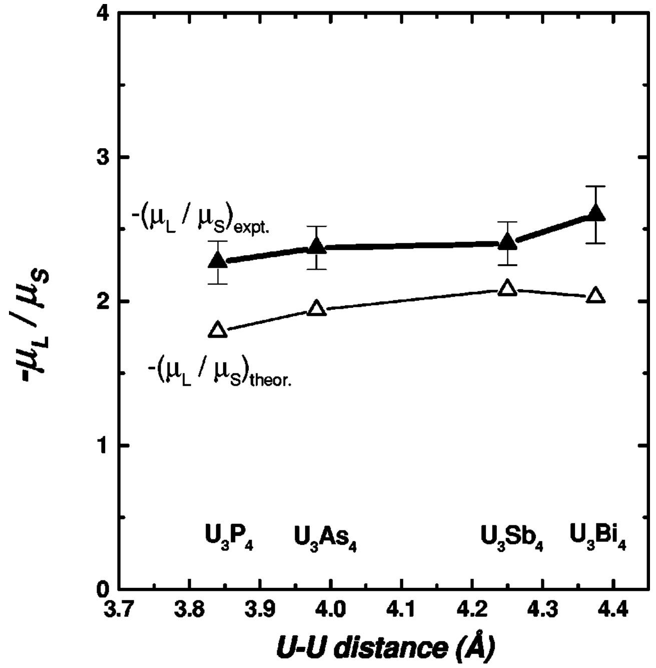

FIG. 2. Comparison of experimental and theoretical (Refs. 19,23) values of the $-\mu_L/\mu_S$ ratio for U_3X_4 series. Values for U_3Sb_4 and U_3Bi_4 are averaged on both sublattices.

The dependence of experimental and theoretical values of the $-\mu_L/\mu_S$ ratio on $d_{\text{U-U}}$ is shown in Fig. 2. Theoretical values of the $-\mu_L/\mu_S$ are considerably smaller than measured, i.e., the hybridization is smaller than that resulting from band calculations. Experimental $-\mu_L/\mu_S$ ratios for two sublattices in antimonide are significantly different, indicating an important role of the local symmetry in the hybridization. A similar effect is present in bismuthide but it is weaker as the corresponding difference in the ratios of the spin and orbital components is much smaller.

Since all uranium sites are symmetrically equivalent, the different hybridization of their $5f$-electron states does not seem to have any physical justification. On the other hand an anisotropy of the hybridization has been suggested for another ferromagnetic uranium compound, UAsSe.[25] In the case of this compound, the tetragonal symmetry of the crystal structure would intrinsically lead to such an anisotropy. In U_3X_4-type pnictides, the local tetragonal symmetry might cause similar anisotropy, where the delocalization of $5f$ states would be different along the local symmetry axis than in the plane perpendicular to that axis. Although anisotropy of all equivalent U ions would be the same, the orientation of its axis would be different for each sublattice. It would cause not only different reduction of the moment, but also different $-\mu_L/\mu_S$ ratios on two sublattices.

All these results combined with the corrected, very small, noncollinearity angle values for U_3P_4 and U_3As_4, show that the local symmetry of U-ions neighborhood has a very significant influence on the hybridization of $5f$ states and, consequently, on the magnetic structure in U_3X_4 series.

We are indebted to K. Knöpfle, L. M. Sandratskii, and J. Kübler for the results of their still unpublished *ab initio* calculations of the magnetic structure in U_3Bi_4.[23] The stay of P.W. at LLB was supported via PECO Extension of the Human Capital and Mobility - Access to Large Scale Facilities Program (Contract No. ERB CIPD CT 940080).

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