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## Polarized neutron diffraction study of spin and orbital moments in UAsSe

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**Abstract.** Unpolarized and polarized neutron diffraction experiments have been performed on a single crystal of tetragonal UAsSe. The measured magnetic form factor corresponds well to that theoretically predicted for a U<sup>4+</sup> ion.

The separation of contributions from the spin ( $\mu_S$ ) and orbital ( $\mu_L$ ) moment yielded values of  $-0.65(9)$  and  $2.07(5)$   $\mu_B$ , respectively, giving the total magnetic moment of  $1.42(4)$   $\mu_B$  at the uranium site compared to the  $1.29(2)$   $\mu_B$  per U atom obtained from magnetization measurements. The  $-\mu_L/\mu_S$  ratio equal to  $3.2(4)$  indicates that the hybridization of 5f electron states with conduction band states is rather weak.

### 1. Introduction

UAsSe crystallizes in the PbFCl-type tetragonal structure ( $P4/nmm$  space group), consisting of layers stacked along the  $c$ -axis in a sequence As–U–Se–Se–U–As, as shown in figure 1, and orders ferromagnetically below 113 K, with an easy magnetization axis parallel to the four-fold symmetry axis ( $c$ -axis). The value of the magnetic moment,  $1.5(1)$   $\mu_B$  per U-atom, found in neutron diffraction experiments on polycrystalline samples [1] was slightly higher than the  $1.36$   $\mu_B$  given by a magnetization experiment on a single crystal [2].

Recently, in search of an origin of striking Kondo-type behaviour of electrical resistivity in stoichiometric UAsSe, we have extensively examined the resistivity and magnetoresistivity of UAs<sub>1-x</sub>Se<sub>1+x</sub> solid solutions ( $0 \leq x \leq 0.06$ ). Thorough x-ray and transmission electron microscopy examinations were also performed. The four-circle neutron diffraction experiment on the single crystal of UAsSe revealed that possibly about 6% of As and Se anions mutually exchange their positions [3]. Such a result favoured the multi-level tunnelling system, rather than the multi-channel Kondo system, as a proper model for the resistivity behaviour.

The presence of hybridization of 5f electron states with the conduction band electron states was established in UAsSe by a study of magneto-optical Kerr spectra [4]. Analysis of these spectra, using first-principles band-theory calculations [5], suggested the possibility of a strong anisotropy of this hybridization: 5f electrons would be delocalized in  $ab$ -planes but localized along the  $c$ -axis. Regarding the layered arrangement of uranium ions in the elementary cell of this compound, such an assumption is fully justified. This anisotropy should also be visible in the magnetic form factor of uranium ions (as magnetic amplitude dependence on the angle

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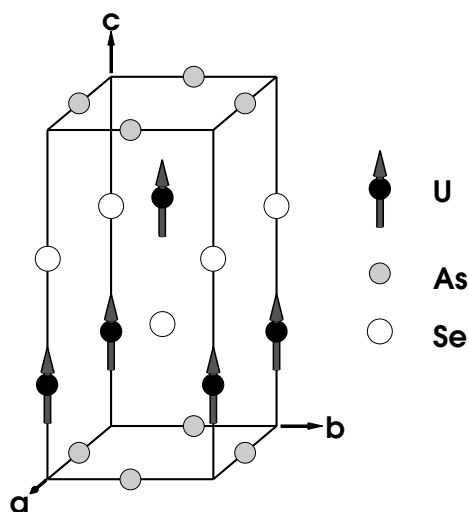


Figure 1. Crystal and magnetic structure of UAsSe.

between the scattering vector,  $\mathbf{Q}$ , and the magnetization vector), which turned our attention to the polarized neutron measurements.

In this work we present results obtained by unpolarized and polarized neutron diffraction, which allowed us to separate the spin,  $\mu_S$ , and orbital,  $\mu_L$ , contributions of the uranium magnetic moment, estimate the hybridization of 5f states and analyse the anisotropy of the uranium magnetic form factor related to its intra-plane and inter-plane delocalization.

## 2. Experiment

Crystals of UAsSe were grown by the chemical vapour transport method as described in [3]. One good quality single crystal of dimensions  $2 \times 2 \times 0.5 \text{ mm}^3$  (along  $a$ -,  $b$ - and  $c$ -axes, respectively) was chosen for the neutron scattering study. Neutron diffraction measurements were carried out at the reactor *ORPHÉE*, LLB CEA, Saclay.

Integrated intensities were collected at room temperature, on the four-circle *6T2* diffractometer. Neutrons of wavelength  $\lambda = 0.9 \text{ \AA}$  ((220) copper monochromator) were used. Polarized neutron flipping ratios were measured on the two-axis lifting-counter diffractometer *5CI* using the wavelength of  $\lambda = 0.845 \text{ \AA}$  (Heusler alloy monochromator). The polarization of the incident neutron beam was  $P_0 = 0.91$ . In both cases the primary beam collimation of  $50'$  was used and higher order contaminations were suppressed to less than 0.01% by means of erbium filters.

Programs *MAGLSQ*, *POLSQ* and *SORGAM* of the Cambridge Crystallography Subroutine Library [6] were used for the refinement on the measured structure factors, the refinement on flipping ratios and the calculation of magnetic amplitudes, respectively. The quality of refinement was characterized by standard quantities:

$$R = \frac{\sum |G_o - G_c|}{\sum G_o} \quad R_W = \frac{\sum w|G_o - G_c|}{\sum wG_o} \quad (1)$$

$$\text{GoF} = \sqrt{\frac{\sum w(G_o - G_c)^2}{N_o - N_v}} \quad w = 1/\sigma^2$$

where  $G_o$  and  $G_c$  are observed and calculated structure factors or flipping ratios and  $\sigma$  is an experimental error (of  $G_o$ ).  $N_o$  and  $N_v$  denote numbers of observations and of variables in the refinement, respectively.

Radial integrals  $\langle j_0 \rangle$  and  $\langle j_2 \rangle$ , as given in [7], were used in an analytical dipole approximation of the magnetic form factor for the  $U^{4+}$  ion in the refinement of the magnetic structure.

### 3. Results

#### 3.1. Magnetization

The magnetization along the  $c$ -axis was measured on two single crystals (weight: 43.7 and 34.95 mg) obtained in the same synthesis as the crystal used for neutron diffraction experiments, which has allowed the reliable comparison of the magnetic moment values determined by the different experimental techniques. Measurements were performed on a SQUID magnetometer at two temperatures: 1.75 K and 3.8 K, and in magnetic fields of up to 4 T. The moment measured at zero external field was found to be  $1.29(2) \mu_B$  per uranium atom and was the same for both crystals (with the accuracy of 0.5%). When the field was increased up to 4 T, the moment value increased by 1%. The values of the moment were identical at both temperatures. It is well known that magnetic and electronic properties of uranium pnicto-chalcogenides are strongly sample dependent. This can explain the difference of magnetization determined in this work and that from [2].

#### 3.2. Unpolarized neutron diffraction

Integrated intensities of 516 reflections were measured. The results of a refinement on their averaged structure factors are presented in table 1 and confirmed that the sample was of good stoichiometry. The extinction correction was applied according to the Becker and Coppens Lorentzian model [8]. The value of the mosaic spread  $g = 0.13 \times 10^{-4} \text{ rad}^{-1}$ , refined for the average domain radius of  $10 \mu\text{m}$ , confirmed a good quality of the crystal. The dependence of the refinement quality on the As and Se site occupation was tested (with the UAsSe stoichiometry preserved.) Both  $R_w$  and GoF varied slightly but continuously. A model with an anion disorder, assuming 6.25% of As atoms mutually exchanging their positions with Se atoms, yielded the best quality of refinement:  $R = 6.72\%$ ,  $R_w = 5.17\%$  and GoF = 2.45, but all refined structure parameters were, within accuracy limits, identical with these shown in table 1, refined for the model of a fully ordered structure. Both adjustable structural parameters:  $z$  of U and  $z$  of Se, as well as an anisotropy of the Debye–Waller temperature factor for As, agree well with those previously obtained by x-ray measurements [3].

#### 3.3. Polarized neutron diffraction

Polarized neutron flipping ratios were measured at 5 K with a vertical magnetic field of 2 T applied nearly parallel to the  $c$ -axis of the sample. (In fact a misalignment of about 5 degrees existed between the  $c$ -axis and the magnetic field direction.) A total of 181 flipping ratios were measured up to  $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$ . The averaging of the measured flipping ratios ( $R_F$ ) on symmetry-equivalent reflections was performed giving 49 independent reflections. The extinction correction was performed with average domain radius of  $10 \mu\text{m}$  and mosaic spread of  $0.13 \times 10^{-4} \text{ rad}^{-1}$ . The dipole-approximation of the magnetic form factor ( $f_U(Q) = \langle j_0(Q) \rangle + C_2 \langle j_2(Q) \rangle$ ) for  $U^{4+}$  ions was used for all  $R_F$ . Results of this refinement are shown in table 2. For many uranium compounds the  $-\mu_L/\mu_S$  decreases below

**Table 1.** The results of refinement on structure factors collected on UAsSe at 300 K. The anisotropic Debye–Waller factor is described by:  $\exp(-\frac{1}{4}(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+\dots+2u_{23}k^2b^{*2}l^2c^{*2}+\dots))$ .

Measured reflections:	516
Independent reflections:	286
$\lambda$	0.9 Å
$\sin \theta/\lambda$	$<0.96 \text{ \AA}^{-1}$
Index ranges:	$-7 < h, k < 7;$ $-12 < l < 12$
U $z$	0.270 06(13)
Se $z$	0.631 69(14)
U $u_{11} = u_{22}$	0.770(26)
U $u_{33}$	0.697(36)
As $u_{11} = u_{22}$	1.177(33)
As $u_{33}$	0.523(38)
Se $u_{11} = u_{22}$	0.757(27)
Se $u_{33}$	0.723(35)
$g [10^{-4} \text{ rad}^{-1}]$	0.130(17)
$R$	6.75%
$R_W$	5.22%
GoF	2.46

**Table 2.** The results of refinement on flipping ratios measured for UAsSe.

Measured $R_F$ :	181
Independent $R_F$ :	49
$\lambda$	0.845 Å
$\sin \theta/\lambda$	$\leq 0.78 \text{ \AA}^{-1}$
$(\mu_S + \mu_L) [\mu_B]$	1.42(4)
$\mu_L [\mu_B]$	2.07(5)
$\mu_S [\mu_B]$	-0.65(9)
$C_2$	1.46(7)
$-\mu_L/\mu_S$	3.2(4)
$R_W$	1.65%
GoF	1.31

3.0 (its value for a free  $U^{4+}$  ion), which is considered to be due to the hybridization of f states. The value of 3.2(4) for this ratio in UAsSe indicates very weak hybridization.

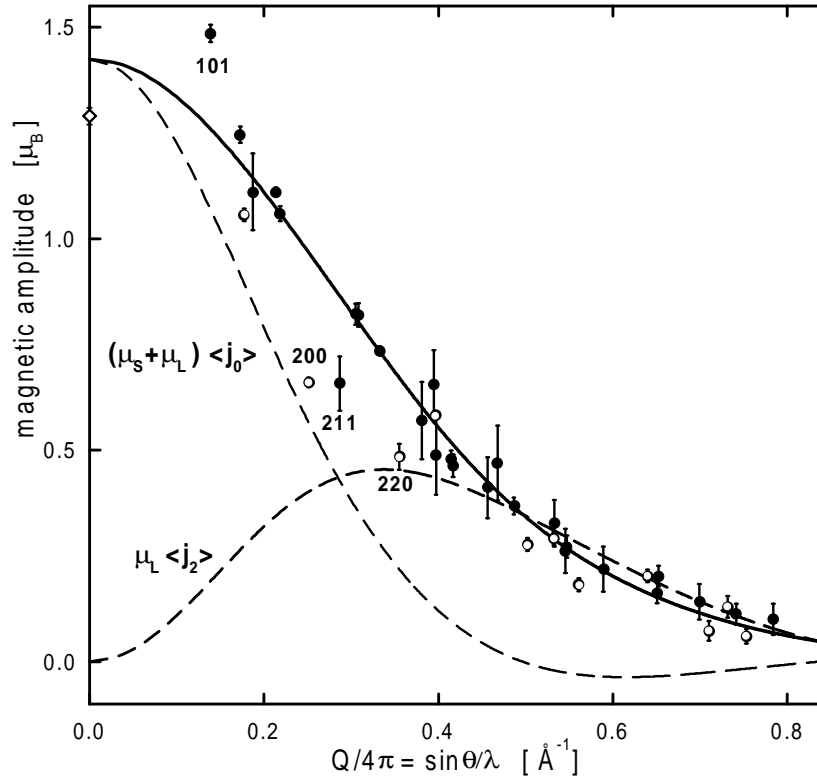
Since the crystal structure of UAsSe is centrosymmetric, both nuclear,  $F_N(\mathbf{Q})$ , and magnetic,  $F_M(\mathbf{Q})$ , structure factors are real quantities and  $F_M(\mathbf{Q})$  can be calculated from the measured flipping ratios:

$$R_F = \frac{1 + 2P_0 \sin^2 \alpha \gamma + \sin^2 \alpha \gamma^2}{1 - 2P_0 \sin^2 \alpha \gamma + \sin^2 \alpha \gamma^2} \quad \gamma = \frac{F_M}{F_N} \quad (2)$$

using the  $F_N$  values of the structure determined in the four-circle diffraction experiment ( $\alpha$  is the angle between the magnetization and the scattering vector  $\mathbf{Q}$ ). To obtain the magnetic form factor of uranium, the observed magnetic scattering amplitudes should be compared to those calculated on the assumption that all of the moment is localized on the U sites. In this approximation we have

$$F_M(\mathbf{Q}) = \sum \exp(i\mathbf{Q} \cdot \mathbf{r}_U) \exp(-W_U)(\mu_U f_U(\mathbf{Q})) \quad (3)$$

where the  $\mathbf{r}_U$  denotes the positions of U atoms,  $W_U$  the Debye–Waller temperature factor and  $\mu_U f_U(\mathbf{Q})$  the uranium magnetic scattering amplitude. The magnetic scattering amplitudes



**Figure 2.** The magnetic amplitudes of uranium ions in UAsSe. Empty and full circles represent in-plane and off-plane reflections, respectively. The solid line is the magnetic amplitude calculated with the  $U^{4+}$  5f form factor taken in the dipole approximation. Dashed lines show moment components proportional to  $(\mu_S + \mu_L) \langle j_0 \rangle$  and to  $\mu_L$ . A diamond represents a value of the moment from the magnetization measurement.

$\mu_U f_U(Q)$  for 37 reflections obtained using equation (3) are shown in figure 2 versus the length of their scattering vectors. The solid line in this figure represents the magnetic amplitudes calculated using the uranium magnetic form factor in the dipole approximation

$$\mu_U f_U(Q) = (\mu_S + \mu_L) f_U(Q) = (\mu_S + \mu_L) \langle j_0(Q) \rangle + \mu_L \langle j_2(Q) \rangle \quad (4)$$

and the refined values of magnetic moments from table 2 ( $(\mu_S + \mu_L) = 1.42 \mu_B$  and  $\mu_L = 2.07 \mu_B$ ).

It is clearly seen that the magnetic amplitudes of four reflections (101, 200, 211 and 220) do not correspond sufficiently well to the calculated values. On the other hand, the amplitudes for the other 33 reflections lie reasonably close to the theoretical curve. The refinement performed on these 33 reflections did not change significantly the values of the refined moment ( $\mu_S + \mu_L = 1.42(4) \mu_B$ ;  $\mu_L = 2.08(5) \mu_B$ ).

#### 4. Anisotropy of form factor

Since a strong anisotropy of 5f electron hybridization in UAsSe was suggested in [5], we tested how the magnetic form factor depended on  $\alpha$ —the angle between the scattering vector  $Q$  and

the magnetization direction (the  $c$ -axis here). First the uranium form factor was extended with an  $\alpha$ -dependent term in the following form:

$$f_U(Q) = \langle j_0(Q) \rangle + (C_2 + \Delta C_2 \cos^2 \alpha) \langle j_2(Q) \rangle. \quad (5)$$

The term  $\Delta C_2 \cos^2 \alpha \langle j_2(Q) \rangle$  in the form factor represents a quadrupolar moment of 5f electron magnetization [9]. The fitting of magnetic amplitudes of all 37 independent  $R_F$  yielded the values:  $C_2 = 1.13$  and  $\Delta C_2 = 0.409$  and practically the same values of  $\mu_S$  and  $\mu_L$ . The quality of this fit, however, was not significantly better than in the case when the form factor in the dipole approximation was used. Another indication of the smallness of the form factor anisotropy in UAsSe follows from the refinement performed on the flipping ratios of the 9 ( $hk0$ ) reflections in the plane perpendicular to the magnetization axis (after rejecting 200 and 220 reflections), which has given:  $(\mu_L + \mu_S) = 1.28(13) \mu_B$  and  $\mu_L = 2.10(11) \mu_B$ , showing within the accuracy limit the same moment values as those refined on all 49 flipping ratios without any anisotropy.

## 5. Discussion and conclusions

It is known that the refinement using  $\langle j_0 \rangle$  and  $\langle j_2 \rangle$  for different ions ( $U^{3+}$ ,  $U^{4+}$  and  $U^{5+}$ ) does not allow the determination of the U ionization state because the radial integrals for both states are very similar [10]. In contrast the value of the ratio  $-\mu_L/\mu_S$  is very sensitive to the ionization state of U. As seen from table 2, within the dipole approximation of the  $U^{4+}$  5f form factor, the spin and orbital components of the magnetic moment on the uranium site were found to oppose each other and have the values:  $\mu_S = -0.65 \mu_B$  and  $\mu_L = 2.07 \mu_B$ . These values are to be compared with the band theory values for these components  $\mu_S = -1.76 \mu_B$ ,  $\mu_L = 2.63 \mu_B$  and  $-\mu_L/\mu_S = 1.49$  [5]. The last value (1.49) for the  $-\mu_L/\mu_S$  ratio predicted by the band theory appeared to be considerably reduced compared not only to the  $U^{4+}$  free ion value ( $-\mu_L/\mu_S = 3$ ) but even to that of the  $U^{3+}$ -ion value (2.33). Surprisingly the experimental value  $-\mu_L/\mu_S = 3.2$  obtained from the refinement favours clearly the 4+ ionization state, which indicates rather weak hybridization of 5f electrons.

We should note as well the rather small value of the form factor anisotropy  $\Delta C_2 = 0.4$  (e.g. compared to 1.3 observed for PuSb [9]). This indicates that the observed anisotropy could have another character, for instance of the 6d type. The  $\langle j_0 \rangle$  radial integral for 6d electrons calculated in [10] decreases very rapidly with increasing of  $Q$  and almost disappears at  $Q/4\pi = 0.2$ . The addition of a term containing this integral to the 5f form factor could justify higher values of magnetic amplitudes in the small- $Q$  range, namely for (101) and (102) reflections. Very similar behaviour was observed in two mixed valence compounds, CeSn<sub>3</sub> and CePd<sub>3</sub> [11]. Their paramagnetic (field-induced) form factors were significantly enhanced in the small  $Q$  range, which was ascribed to the presence of a strong 5d component in the 4f electron wavefunction. Unfortunately, for the uranium compounds such an explanation does not hold because, owing to a wide spatial extent of the 6d electron wavefunctions, the 6d electrons have no orbital moment and should have their spin moment oriented parallel to the spin moment of the 5f electrons, thus antiparallel to the total moment on uranium site. This is in contrast with our results since the total moment of U at small  $Q$  should be diminished but not enhanced.

The variation of four reflections from a smooth form factor curve might be due to the inadequacy of our extinction corrections, or to the presence of multiple scattering. Indeed we observed multiple scattering in the four-circle measurements: for instance the reflection (100), forbidden in the PbFCI structure, had a small but non-zero intensity when measured

in bisecting geometry. Its intensity disappeared when the crystal was rotated around the scattering vector (so called  $\psi$ -rotation changing conditions of the multiple scattering.) Since the two-axis geometry of the polarized neutron diffractometer does not allow such crystal rotation, we were not able to eliminate this error in the flipping ratio measurement. However, in our opinion, neither multiple scattering nor extinction can explain the observed deviation of the four reflections from the smooth form factor curve. In fact, the presence of multiple scattering should lead to the appearance of systematic errors in weak reflections while the extinction problem manifests itself in the strong reflections. Since among the four reflections under consideration both strong and weak reflections are present, it looks improbable that a correction could be found being able to bring all the four reflections on a smooth curve, simultaneously.

The most probable reason for the discrepancy can be due to the fact that the magnetic amplitudes shown in Figure 2 have been obtained assuming that all of the magnetic moment is concentrated on the uranium site, thus neglecting completely the f-p hybridization. In reality the Fourier difference maps constructed from the observed and calculated magnetic amplitudes indicated that some negative density might exist at the As and the Se sites. Unfortunately the Fourier synthesis with such a limited data set is rather unreliable. Our attempts to refine a model with the magnetic moments at the As and the Se sites were also unsuccessful since no information was available on a possible space distribution (magnetic form factor) of such moments.

In conclusion, we believe that the minor discrepancies mentioned above do not influence our essential result concerning the orbital- to spin-moment ratio and these results clearly indicate a very weak (if any) hybridization of 5f electron states with conduction band states in UAsSe, which inhibits the confirmation of the anisotropy in the delocalization of 5f electrons.

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