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Abstract. We report a high statistic x-ray magnetic circular dichroism study of $USb_{0.5}Te_{0.5}$ carried out at the uranium $M_{IV,V}$ edges. Using the sum rules, the detailed analysis of our data yields orbital and spin moments of the 5f uranium electrons in reasonable agreement with values extracted from a localized moment approach.

The study of uranium compounds is attracting much interest because of the variety of behaviours which can be found at low temperature. Depending on the strength of the hybridization between the 5f electrons of the uranium atoms and the conduction electron band, one finds electronic and magnetic properties with characteristics ranging from typical localized to itinerant electron systems [1]. The behaviour of some anomalous rare earth (Yb, Ce) compounds is similar, but the uranium compounds have their own specificity. The crystal electric field acting on the uranium ions and the spin–orbit coupling have comparable strengths. In addition, when the magnetic properties are characteristic of itinerant systems, the width of the 5f conduction band and the spin–orbit interaction have about the same value. This leads to a sizeable orbital magnetic moment [2].

Recent years have seen a surge of activity in the use of photon beam techniques to study magnetic properties of materials [3]. Among all the experimental techniques currently developed (magnetic x-ray diffraction, magnetic Compton scattering, resonant Raman scattering and magnetic circular dichroism at absorption edges) the latter technique has the great advantage that both orbital ($\mu_L = -\langle L_z \rangle \mu_B$) and spin ($\mu_S = -2\langle S_z \rangle \mu_B$) magnetic moments of each electron shell for each ion species of a ferromagnet can be determined, in principle easily, using sum rules [4, 5]. Experiments on metallic iron and cobalt have nicely confirmed this potential application [6].

The investigation of the uranium 5f electrons of a ferromagnet by x-ray magnetic circular dichroism (XMCD) can be performed using either the $M_{IV,V}$ or $N_{IV,V}$ edges located at

3.73 keV, 3.55 keV and 0.78 keV, 0.73 keV, respectively [7]. These edges involve the $3d_{3/2,5/2} \rightarrow 5f$ and $4d_{3/2,5/2} \rightarrow 5f$ electronic transitions, respectively. In this work we report XMCD measurements carried out at the uranium $M_{IV,V}$ edges of $USb_{0.5}Te_{0.5}$. Although this type of measurement presents much interest, only one previous measurement has been done [8]. The main reason seems to be the very small number of spectrometers available for performing these measurements.

For this XMCD study on an uranium compound carried out at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) we have chosen to investigate $USb_{0.5}Te_{0.5}$, a member of the $USb_{1-x}Te_x$ group of solid solutions, whose magnetic properties are characteristic of a localized ferromagnet (USb is an antiferromagnet and UTe a ferromagnet recently speculated to be a mixed valence system [9]). This compound crystallizes in the NaCl-type structure, and orders ferromagnetically at $\sim$200 K with the uranium moments lying along the [111] body diagonal. The saturated magnetic moment of the uranium atom has a value of $\sim 2.6 \mu_B$ [10]. The uranium electronic configuration can be considered as purely ionic with the 5f electron count $n_{5f} = 3$. Therefore the sum rules should be applicable [4, 5].
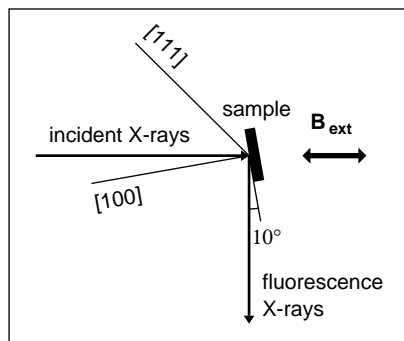

Figure 1. Schematic top view of the experiment.

The XMCD measurements have been performed at the spectrometer of beamline ID12A which is dedicated to polarization-dependent x-ray absorption studies [11]. The x-ray source was the helical undulator Helios II which emits x-ray radiation with a high and flexible polarization [11]. The first harmonic of the undulator was selected to cover the energy range from 3.50 keV to 3.85 keV. The fixed-exit double-crystal monochromator was equipped with a pair of Si (111) crystals. The spectra were recorded in fluorescence yield mode using a Si photodiode associated with a digital lock-in exploiting the modulation of the x-ray beam [12]. The data were recorded on a $\sim 4 \times 4 \times 2$ mm^3 $USb_{0.5}Te_{0.5}$ single crystal at 100 K and in a 2 T magnetic field produced by a superconducting magnet. In crystals such as $USb_{0.5}Te_{0.5}$ the (001) planes are cleavage planes. The experimental geometry is shown in figure 1. The sample was mounted such that the incident beam was 10° off the [100] direction in the plane defined by the [100] and [111] axes. The incident and fluorescent x-ray beams subtended the illuminated crystal face at angles $\alpha = 80°$ and $\beta = 10°$, respectively. The magnetic field was applied along the incident beam. Within these experimental conditions, the projection of the total magnetic moment along the field direction is $\sim 1.8 \mu_B$.

The relative direction of the field to the light helicity was selected by changing either the direction of the field or helicity of the x-ray after each energy scan (roughly every 15
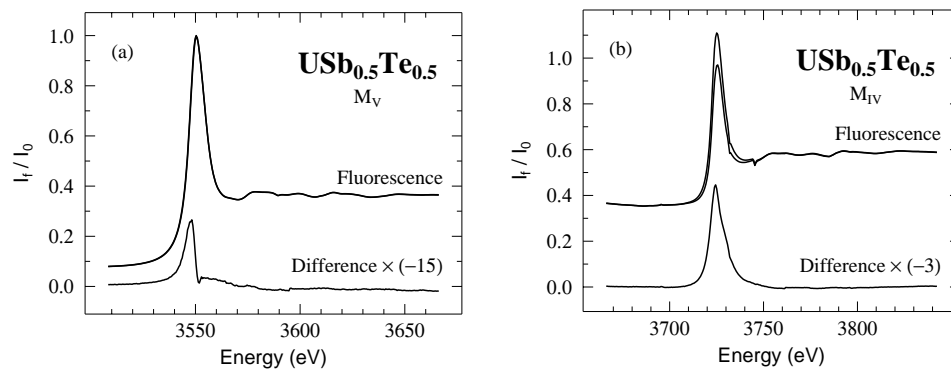
Figure 2. Fluorescence spectra and dichroic asymmetries ΔI ($\Delta I = I_+ - I_-$) measured on USb$_{0.5}$Te$_{0.5}$ at the M$_{IV,V}$ edges of uranium. The intensity of the applied magnetic field was 2 T and the temperature 100 K. The index $+$ ($-$) specifies that the applied field is parallel (antiparallel) to the x-ray helicity. The origin of the ordinate scale for the fluorescence spectra is arbitrary.

minutes). Within uncertainties, the resulting dichroic spectra were the same.

In figure 2 we present the normalized fluorescence spectra $I_+(E)$ and $I_-(E)$ and the associated dichroic asymmetry for the two edges. We did not apply any correction to the measured spectra and asymmetries. We define $I(E) \equiv I_f(E)/I_0(E)$ where $I_f(E)$ is the measured fluorescence intensity and $I_0(E)$ is proportional to the incident flux. The index $+$ ($-$) specifies that the magnetic field is parallel (antiparallel) to the x-ray helicity. The two dichroic signals are positive, indicating a strong orbital magnetic moment [4]. Their ratio is ~ 8, with the signal weaker at the M$_V$ edge. The shapes of the two dichroic signals are quite distinct. Whereas the maxima of the fluorescence and dichroic asymmetry occur at about the same energy for the M$_{IV}$ edge, they are shifted by ~ 2.0 eV at the M$_V$ edge, the maximum of the dichroic asymmetry being at the lower energy. We note the extended x-ray fine stucture (EXAFS) between the two edges.

Although the use of fluorescence yield detection as a method to study quantitatively the x-ray absorption is questionable [13–16], it has been shown recently that, in the presence of a crystal field or of strong core–hole spin–orbit coupling, the sum rules are still applicable, provided that the fluorescence spectra are corrected for self-absorption [17]. Therefore, since the M$_{IV,V}$ edges of uranium compounds are characterized by a large spin–orbit coupling, we can use the sum rules with confidence.

In order to obtain the absorption and dichroic spectra from the fluorescence data, two steps are required. First we correct the self-absorption effect, converting fluorescence data to absorption coefficients [18]. Next we correct for the dependence of the degree of circular polarization of the monochromatic x-ray beam, which is energy dependent.

We define $I_X(E) \equiv I_{f,X}(E)/I_0(E)$ as the normalized fluorescence spectra produced by a core hole at the energy level X. In our case X is either the 3d$_{3/2}$ or 3d$_{5/2}$ level. For a thick sample such as ours, the absorption coefficient, $\mu_X(E)$, associated with the production of the core hole in the investigated level X is given by [18–20]:

$$\mu_X(E) = \frac{I_X(E)[\mu_0(E) + A]}{B - I_X(E)} \tag{1}$$

where $\mu_0(E)$ describes absorption due to shallower core levels, valence levels and other atomic species and A and B are parameters independent of the energy E. We have defined
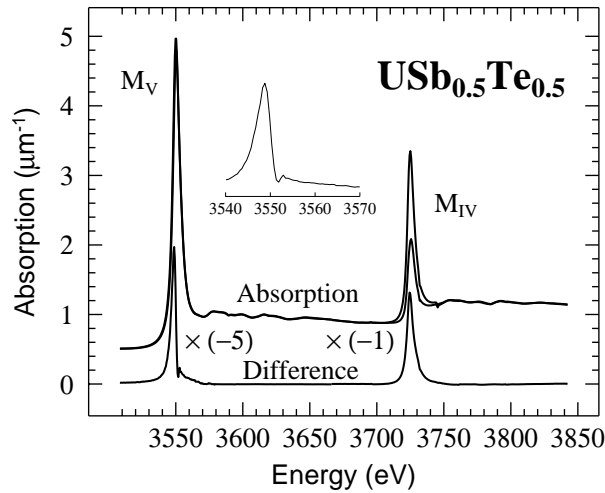
Figure 3. Absorption spectra and associated dichroic asymmetry $\Delta\gamma$ ($\Delta\gamma = \gamma_+ - \gamma_-$) measured at the $M_{IV,V}$ edges of uranium in $USb_{0.5}Te_{0.5}$. The intensity of the applied magnetic field was 2 T and the temperature 100 K. The index $+$ ($-$) specifies that the applied field is parallel (antiparallel) to the x-ray helicity. These spectra have been deduced from the fluorescence spectra corrected for self-absorption and energy dependence of the circular polarization rate of the monochromatic beam. The dichroic spectrum is normalized to 100% circular polarization rate. The inset shows the details of the dichroic spectrum at the M_V edge: notice that there is basically no dichroism at energies higher than that of the maximum of the absorption.

$A = g_1\mu_0(E_f)$, where E_f is the energy of the photon resulting from the hole decay and g_1 is a geometrical factor: $g_1 = \sin\alpha / \sin\beta$. $\mu_0(E)$ is computed using atomic data from [21]. B is adjusted so that the isotropic absorption (assuming it is the average of the absorption measured for the two opposite circular polarization states) obtained from fluorescence yield using (1) matches the results from the total electron yield recorded at beamline SU22 of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France) [22]. We carefully reproduced the branching ratio and the ratio between the heights of the white line and the step function accross the edge measured by total electron yield.

The computation of the net circular polarization rate in the monochromatic primary beam is discussed in [23]. Taking account of the circular polarization rate of the beam before the monochromator (~ 0.97) and the monochromator setup we get a computed circular polarization on the sample which varies from $P_2'(3.50 \text{ keV}) = 0.33$ to $P_2'(3.85 \text{ keV}) = 0.47$. The difference between the absorption spectrum for a given circular polarization state and the isotropic spectrum is divided by $P_2'(E)$. The result is then added to the isotropic spectrum to give the absorption for a fully circular polarization.

Figure 3 shows the absorption spectra and the dichroic asymmetry deduced from the fluorescence spectra (figure 2). The absorption correction has substantially modified the spectra (the ratio of the two absorption dichroic signals is only ~ 3.5) but still the maximum of the dichroic signal at the M_V edge is shifted towards lower energy by ~ 1 eV. The dichroic signal at the M_{IV} edge is broader than at the M_V edge. In fact, on the high-energy side of the M_V dichroic asymmetry, an atomic multiplet structure is seen. It is rewarding that even the pure-J multiplet calculations reproduce qualitatively our dichroic asymmetry spectrum [24].

One could imagine fitting our dichroic asymmetry spectrum to a model describing the

trivalent uranium ion interacting with the x-ray beam and taking into account the crystal field produced by the surrounding ions and the molecular field. A much simpler approach is to use the sum rules [4, 5, 17] to estimate the orbital and the orbital-to-spin ratio of the uranium 5f valence electrons. For the case of interest here the sum rules write :

$$\frac{\langle L_z \rangle}{3n_h} = \frac{\int_{M_V + M_{IV}} \Delta\gamma(E)\mathrm{d}E}{\int_{M_V + M_{IV}} \left[\gamma^+(E) + \gamma^-(E) + \gamma^{\mathrm{iso}}(E)\right]\mathrm{d}E} \tag{2}$$

and

$$\frac{\langle L_z \rangle}{2\langle S_e \rangle} = \frac{2\int_{M_V + M_{IV}} \Delta\gamma(E)\mathrm{d}E}{2\int_{M_V} \Delta\gamma(E)\mathrm{d}E - 3\int_{M_{IV}} \Delta\gamma(E)\mathrm{d}E}. \tag{3}$$

$\gamma^{\mathrm{iso}}(E)$ is the isotropic absorption spectrum and n_h is the number of holes in the 5f shell: $n_h \equiv 14 - n_{5f} = 11$. Following Collins *et al* [8] we have defined the effective spin $\langle S_e \rangle \equiv \langle S_z \rangle + 3\langle T_z \rangle$. $\langle T_z \rangle$ is the expected value of the magnetic dipolar operator [5]. Following common practice we write the second sum rule as an orbital-to-spin ratio. This method should minimize systematic errors. From the absorption and associated dichroic asymmetry integrals, we measure $-\langle L_z \rangle/3n_h = 0.091$ and $\langle L_z \rangle/\langle S_e \rangle = -1.89$. The first sum rule gives $\langle L_z \rangle = -3.0$ (2). The main origins for the uncertainty arise from the background determination in the absorption edge signal i.e. absorption not due to $3d_{3/2,5/2}$ $\rightarrow$ 5f transitions, and the intrinsic precision of the sum rules [5]. The correction for self-absorption effects does not significantly contribute to this error bar because we can rely on total electron yield spectra measured on the same compound and this correction affects the spectra recorded for both circular polarization states. From the $\langle L_z \rangle$ value, we obtain a uranium orbital magnetic moment of 3.0 (2) μ_B which is parallel to the applied field and therefore has the same direction as the uranium total magnetic moment. In intermediate coupling, valid for 5f electrons, a calculation gives $\langle T_z \rangle/\langle S_z \rangle = 0.62$ [24]. Then we deduce $\langle S_z \rangle = 0.56$ (5), i.e. the uranium ion carries a spin moment of 1.1 (1) μ_B antiparallel to the orbital moment. Therefore the total uranium moment ($\sim 1.9\mu_B$) extracted from the sum rules fits well the expected uranium moment ($\sim 1.8\mu_B$) within our experimental conditions. It is worth noticing that the ratio $-\mu_L/\mu_S = 2.68$ is in close agreement with the value (2.60) expected for a pure U^{3+} ionic state [24] and with those deduced from polarized neutron scattering results in the parent compounds USb and USb$_{0.8}$Te$_{0.2}$ [25].

In conclusion, we have reported an x-ray magnetic circular dichroism study performed at the European Synchrotron Radiation Facility on USb$_{0.5}$Te$_{0.5}$ for which the uranium is in the ionic 3+ state. Using the sum rules, the detailed analysis of the data yields orbital and spin magnetic moments of the 5f uranium electrons in reasonable agreement with values extracted from a localized moment approach.

Recently, the ferromagnet UFe$_2$ has been investigated by the same technique as USb$_{0.5}$Te$_{0.5}$ [26]. In agreement with neutron results and band structure calculations, it has been found that the orbital and spin moments are antiparallel and virtually cancel the U sublattice magnetization.

References

[1] Freeman A J and Lander G H (eds) 1984, 1985 and 1989 *Handbook on the Physics and Chemistry of the Actinides* vol 1, 2 and 5 (Amsterdam: North-Holland)
    Gschneidner K A Jr, Eyring L, Lander G H and Choppin G R (eds) 1993 and 1994 *Handbook on the Physics and Chemistry of Rare Earths* vol 17 and 19 (: Elsevier)
[2] Lander G H, Brooks M S S and Johansson B 1991 *Phys. Rev.* B **43** 13 672
[3] Lovesey S W 1993 *Rep. Prog. Phys.* **56** 257

[4] Thole B T, Carra P, Sette F and van der Laan G 1992 *Phys. Rev. Lett.* **68** 1943

[5] Carra P, Thole B T, Altarelli M and Wang X 1993 *Phys. Rev. Lett.* **70** 694

[6] Chen C T, Idzerda Y U, Lin H-J, Smith N V, Meigs G, Chaban E, Ho G H, Pellingrin E and Sette F 1995
     Phys. Rev. Lett. **75** 152

[7] Kalkowski G, Kaindl G, Brewer W D and Krone W, 1987 *Phys. Rev.* B **35** 2667

[8] Collins S P, Laundy D, Tang C C and van der Laan G 1995 *J. Phys.: Condens. Matter* **7** 9325

[9] Trygg J, Wills J M, Brooks M S S, B Johansson and Eriksson O 1995 *Phys. Rev.* B **52** 2496

[10] Rossat-Mignod J, Burlet P and Lander G H 1984 1995 *Handbook on the Physics and Chemistry of the
     Actinides* vol 1 ed A J Freeman and G H Lander (Amsterdam: North-Holland) p 415

[11] Goulon J, Brookes N B, Gauthier C, Goedkoop J, Goulon-Ginet C, Hagelstein M and Rogalev A 1995
     Physica B **208/209** 199

[12] Gauthier C, Goujon G, Feite S, Moguiline E, Braicovich L, Brookes N B and Goulon J 1995 *Physica* B
     208/209 232

[13] Strange P, Durham P J and Gyorffy B L 1991 *Phys. Rev. Lett.* **67** 3590

[14] Hague C F, Mariot J-M, Strange P, Durham P J and Gyorffy B-L 1993 *Phys. Rev.* B **48** 3560

[15] Duda L-C, Stöhr J, Mancini D C, Nilsson A, Wassdahl N, Nordgren J and Samant M G 1994 *Phys. Rev.* B
     50 16758

[16] de Groot F M F, Arrio M A, Sainctavit Ph, Cartier Ch, and Chen C T 1994 *Solid State Commun.* **92** 991

[17] Michel van Veenendaal, Goedkoop J B and Thole B T 1996 *Phys. Rev. Lett.* **77** 1508

[18] Sparks C J 1990 *Synchrotron Radiation Research* ed H Winick and S Doniach (New York: Plenum) 1980
     p 459

[19] McWhan D B, Vettier C, Isaacs E D, Ice G E, Siddons D P, Hastings J B, Peters C and Vogt O 1990 *Phys.
     Rev.* B **42** 6007

[20] Eisebitt S, Böske T, Rubensson J-E and Eberhardt W 1993 *Phys. Rev.* B **47** 14 103

[21] Storm E and Israel H I 1970 *Nuclear Data Tables A* **7** 565

[22] Finazzi M, Dias A-M, Sainctavit Ph, Kappler J-P, Krill G, Sanchez J P, Dalmas de Réotier P, Yaouanc A
     and Vogt O unpublished

[23] Malgrange C, Carvalho C, Braichovich L and Goulon J 1991 *Nucl. Instrum. Methods* A **308** 390

[24] Gerrit van der Laan and Thole B T 1996 *Phys. Rev.* B **53** 14 458

[25] Lander G H 1993 *Handbook on the Physics and Chemistry of Rare Earths* vol 17 ed K A Gschneidner Jr *et al*
     (:Elsevier) p 635

[26] Finazzi M, Sainctavit Ph, Dias A-M, Kappler J P, Krill G, Sanchez J P, Dalmas de Réotier P, Yaouanc A,
     Rogalev A and Goulon J 1997 *Phys. Rev.* B **55** 3010