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Orbital and spin moments in uranium compounds from X-ray magnetic circular dichroism

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Abstract

The knowledge of the orbital (μ_L) and spin (μ_S) magnetic moments of a magnetic material is fundamental for the understanding of its basic properties. X-ray Magnetic Circular Dichroism (XMCD) at the uranium M-edges (3.5–3.8 keV) of a ferromagnet is a new tool which provides a direct and independent determination of μ_L and μ_S using sum rules. Here we report on recent XMCD experiments performed on uranium compounds with different degree of hybridization $USb_{0.5}Te_{0.5}$ (localized), UFe_2 (strongly hybridized) and US (weakly hybridized). The results are compared to those obtained from the analysis of the magnetic form factor deduced from neutron scattering experiments. The importance of the value assigned to the magnetic spin dipolar operator $\langle T_z \rangle$ is emphasized.

Keywords: Uranium compounds; Magnetism; Orbital and spin moments; X-ray absorption spectroscopy

1. Introduction

For the condensed matter physicist, actinide compounds are attractive because they exhibit very different magnetic behavior such as Pauli paramagnetism, localized and itinerant magnetism, Kondo effect and heavy fermion [1]. Although the f electrons of these systems are generally treated in a localized magnetism framework, one encounters compounds, especially with light actinide elements such as uranium, where the hybridization of f electrons with conduction or ligand electrons leads to properties which are characteristic of an itinerant magnetic system. In such systems one generally expects a strong reduction if not a quenching of the orbital moment. But the actinide compounds have a specificity: the spin–orbit coupling interaction has the same order of magnitude as the width of the 5f band. This can induce a sizeable orbital magnetic moment [2]. Therefore a study of the orbital and spin components of the uranium moment in compounds with different degree of hybridization is expected to be fruitful.

In this study we have chosen to investigate (i) a localized magnet $USb_{0.5}Te_{0.5}$ [3] which is a solid solution between USb and UTe and (ii) a strongly hybridized magnet UFe_2 [4]. In addition, we will compare our results with the one obtained on US [5] which is considered as a weakly hybridized magnet.

2. X-ray magnetic circular dichroism

X-ray Magnetic Circular Dichroism consists of measuring the absorption of a compound for X-rays with the two opposite (left and right) states of circular polarization. Such a technique requires a finite bulk magnetization of the sample: ferromagnets can therefore be studied. The study of the 5f electron shell can be performed by tuning the energy of the X-rays close to the $M_{V,IV}$ edges of uranium (located at 3.552 keV and 3.728 keV, respectively) where electronic transitions between $3d_{3/2,5/2}$ and 5f states are induced. With the recent construction of third generation synchrotrons such as the European Synchrotron Radiation Facility (ESRF), Grenoble, France, specific insertion devices have been designed to produce high flux of X-rays with a degree of circular polarization close to 100% [6]. Furthermore, theoretical developments have shown that the orbital and spin components of the magnetic moment of the final state, namely the 5f shell in our uranium experiments, can be deduced from dichroism measurements. The expectation values $\langle L_z \rangle$ and $\langle S_z \rangle$ of the

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orbital and spin moment operators are related to the areas of the absorption and dichroism spectra through the sum rules [7,8]

$$\frac{\langle L_z \rangle}{3n_h} = \frac{\int_{M_V+M_{IV}} \Delta\gamma(E)\mathrm{d}E}{\int_{M_V+M_{IV}} [\gamma^+(E) + \gamma^-(E) + \gamma^{iso}(E)]\,\mathrm{d}E} \quad (1)$$

and

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

where $\gamma^{\pm}(E)$ is the absorption as a function of energy for left $(+)$ and right $(-)$ circular polarization light, γ^{iso} the isotropic absorption and n_h the number of holes in the 5f shell. $\Delta\gamma \equiv \gamma^+ - \gamma^-$ is the dichroism spectrum and $\langle S_e \rangle \equiv \langle S_z \rangle + 3\langle T_z \rangle$. $\langle T_z \rangle$ is the expectation value of the magnetic dipole operator which describes correlations between the spin and position of each electron. Whereas the first sum rule (Eq. (1)) directly yields $\langle L_z \rangle$, the estimate of $\langle S_z \rangle$ from the second sum rule (Eq. (2)) is more involved because it requires the knowledge of $\langle T_z \rangle$. $\langle T_z \rangle$ is not easily measured, but theoretical computations of its value have been recently published [9].

3. Experimental

$USb_{0.5}Te_{0.5}$ crystallises in the rocksalt (NaCl) structure and undergoes a ferromagnetic transition at ~200 K. The very anisotropic uranium magnetic moment is aligned along the [111] direction of the cubic crystal structure and its low temperature value is ~2.6 μ_B [10]. The uranium electronic configuration is considered to be close to the U^{3+} ($5f^3$) ion one. Therefore $n_h \equiv 14 - n_{5B} = 11$ and the ratio between the orbital ($\mu_L \equiv -\langle L_z \rangle \mu_B$) and spin ($\mu_S \equiv -2\langle S_z \rangle \mu_B$) moment is expected to be -2.60 as computed in the intermediate coupling scheme which is valid for uranium [9]. The experiment was performed on a single-crystalline sample and for experimental reasons the easy axis was mounted ~44 degrees away from the magnetic field direction yielding a projection of the low temperature moment along that axis of ~1.85 μ_B.

UFe_2 crystallises in the FCC Laves phase structure and is ferromagnetic below 160 K. The low temperature magnetic moment per formula unit is ~1.2 μ_B which is decomposed as 2×0.6 μ_B for the Fe atoms and virtually 0 for the U moment. This was nicely demonstrated by a polarized neutron diffraction study of the U ion magnetic form factor [11] which revealed that μ_L and μ_S have about the same magnitude but are of opposite direction (following Hund's third rule): $\mu_L = 0.23$ μ_B and $\mu_S = -0.22$ μ_B and then $\mu_L/\mu_S \simeq -1$. The valency of the U ion has not been clearly determined but n_{5f} is probably 2 or 3. We deduce then $n_h = 11$ or 12. Contrary to $USb_{0.5}Te_{0.5}$, UFe_2 is almost isotropic, and we performed the measurements on a polycrystalline ingot.

The experiments were carried out at the ESRF on the ID12A beamline which is dedicated to polarization dependent X-ray absorption studies. The fixed-exit double-crystal monochromator was equipped with a pair of Si(111) crystals cooled down to -140°C. The polarization rate of the monochromatic beam was estimated to vary between 35% at the M_V edge to 45% at the M_{IV} edge. The XMCD spectra were obtained by the difference of X-ray absorption near-edge structure (XANES) spectra recorded consecutively either reversing the helicity of the incident beam or flipping the magnetic field (± 2 T) generated by a superconducting magnet. This field is used to magnetically polarize the sample.

At the relatively low energy of the uranium $M_{V,IV}$ edges, the absorption coefficient of uranium compounds is very large and a measurement of this coefficient in transmission geometry, i.e. in directly measuring the ratio of the transmitted beam intensity through the sample to the incident beam intensity, would require a very thin sample which is not easily prepared. Instead the measurement of the total fluorescence yield arising from the relaxation of the excited state created by the absorption process is relatively easy and was chosen for these experiments. The fluorescence yield is known to be non-proportional to the absorption because of different effects, e.g. different fluorescence probabilities of the intermediate states, saturation effect, reabsorption of the fluorescence X-rays. We have corrected for these last two effects following standard practice [12]. We also note that a recent theoretical work has shown that the application of sum rules to total fluorescence yield experiments gives satisfactory results in the presence of crystal field or strong core hole spin–orbit coupling [13]. At least the latter condition is met in our uranium experiments.

4. Results and discussion

In Fig. 1 and Fig. 2 are presented the absorption and dichroism spectra recorded for $USb_{0.5}Te_{0.5}$ and UFe_2. It is easily seen that the dichroism signals are much weaker in UFe_2 than in $USb_{0.5}Te_{0.5}$. This reflects that the orbital and spin contribution are about an order of magnitude weaker in the former compound. One also notices that the dichroism signals have the same sign at both edges: with reference to the first sum rule (Eq. (1)) we deduce that the absolute value of the orbital moment is relatively large. This is expected for an uranium compound. The sign of the dichroism signal implies that μ_L is parallel to the bulk magnetization of the sample for both compounds. This is again expected for $USb_{0.5}Te_{0.5}$ since $|\mu_L| > |\mu_S|$ for a U^{3+}

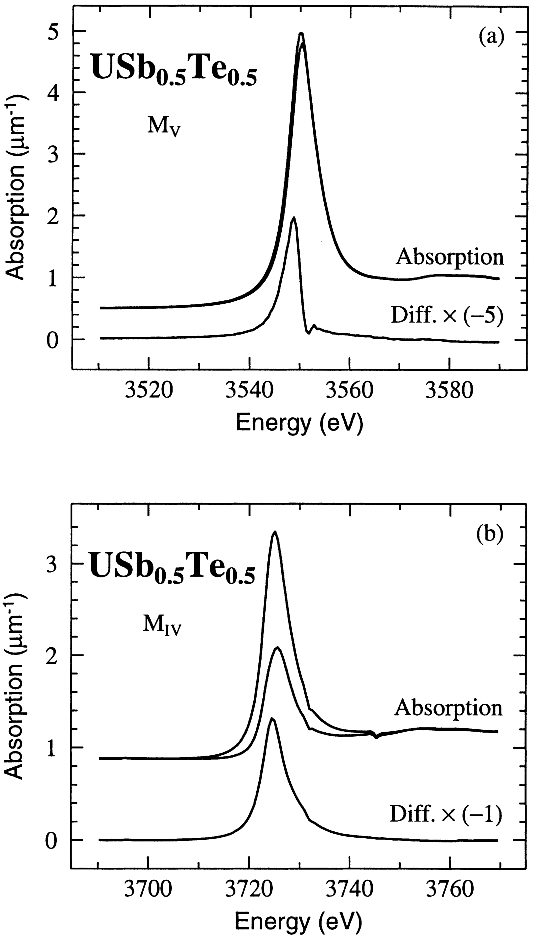

Fig. 1. Absorption spectra recorded on a $USb_{0.5}Te_{0.5}$ single crystal for the two states of circular polarization of the X-ray beam and dichroism (difference) spectrum. The a(b) panel is relative to the M_V, (M_{IV}) absorption edge. The measurements have been performed at 100 K with an external field of 2 T.

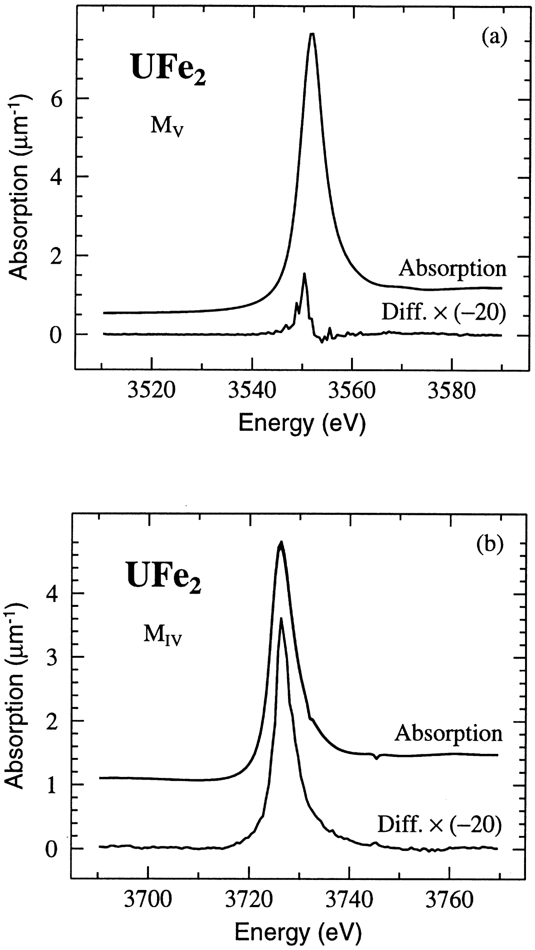

Fig. 2. As for figure 1 but the measurements refer to a UFe_2 polycrystalline ingot at 20 K. Note that the difference between the spectra recorded for the two circular polarization states is so small that the spectra can hardly be distinguished on the figures.

ion and therefore the total magnetic moment μ_T has the same orientation as μ_L. The information is more interesting for UFe_2 since it proves that μ_L is parallel to the bulk magnetization which is determined by the (spin) Fe moment.

The application of the sum rules gives $\langle L_z \rangle = -3.0$ (2) and -0.21 (2) for $USb_{0.5}Te_{0.5}$ and UFe_2 respectively and $\langle L_z \rangle / \langle S_e \rangle = -1.9$ (1) for both compounds. Note that the uncertainty on n_h in UFe_2 (between 11 and 12) results only in an slightly increased error bar on $\langle L_z \rangle$.

We first deal with $USb_{0.5}Te_{0.5}$. We find $\mu_L = 3.0$ (2) μ_B. To extract μ_S from our data, we need information about $\langle T_z \rangle$. In intermediate coupling, valid for 5f electrons, a calculation gives for the U^{3+} ion ($5f^3$) $\langle T_z \rangle / \langle S_z \rangle = 0.62$ [9]. Then we deduce $\langle S_z \rangle = 0.56$ (5), i.e. the uranium ion carries a spin moment $\mu_S = -1.1$ (1) μ_B. The total uranium moment is then $\mu_T = \mu_L + \mu_S \simeq 1.9 \mu_B$ and has the expected value for our experimental arrangement. The ratio $\mu_L / \mu_S \simeq -2.68$ is close to the theoretical prediction for an ionic $5f^3$ configuration.

We now turn to the more difficult case of UFe_2. We find $\mu_L = 0.21$ (2) μ_B in agreement with the result given by polarized neutron scattering [11]. Both band structure calculations [14] and experiments [15] have shown that, in the bulk, the itinerant magnetic systems Fe, Co and Ni are characterized by a ratio $\langle T_z \rangle / \langle S_z \rangle$ (concerning the 3d shell) lower than 0.01. UFe_2 is strongly hybridized and if we take $\langle T_z \rangle = 0$, we get $\langle S_z \rangle = 0.11$ (1) and $\mu_S = -0.22$ (2) μ_B in accord with the neutron data. Taking the theoretical prediction of 1.16 or 0.62 for $\langle T_z \rangle / \langle S_z \rangle$ in either a $5f^2$ or $5f^3$ configuration would have yielded a value for $\langle S_z \rangle$ too small by a factor 4.5 or 2.9.

A third XMCD experiment on a uranium compound is reported in the literature [5]. It was performed on US whose properties are close to the $USb_{0.5}Te_{0.5}$ one. US ($5f^3$ configuration) is nevertheless believed to be weakly hybridized: for instance the experimental value for the ratio $\mu_L / \mu_S \simeq -2.3$ deduced from the analysis of the magnetic form factor of uranium measured by neutron diffraction [16] has an absolute value somewhat reduced compared to the free ion value (2.60). Collins finds a value of μ_L in agreement with the neutron assignment and deduce, combining their data and neutron data, $\langle T_z \rangle / \langle S_z \rangle \simeq 0.60$ close to the prediction for U^{3+} in intermediate coupling [9].

In conclusion XMCD is a powerful tool for investigating the magnetism of an electronic shell of a given ion. We have shown examples of data recorded on different uranium compounds. This technique is found to give reliable estimates for μ_L. The measurement of μ_S is however not so direct because of the coupling of $\langle S_z \rangle$ and $\langle T_z \rangle$ in $\langle S_e \rangle$. With the help of neutron scattering data it is possible to extract $\langle S_z \rangle$ (and μ_S) and $\langle T_z \rangle$. The experimental results presented in this contribution may suggest that $\langle T_z \rangle$ is reduced compared to the free ion value as the 5f uranium electrons are hybridized. More data on a wide range of uranium compounds are needed to confirm this conclusion. We mention that another technique using high energy circularly polarized X-rays, namely magnetic Compton scattering, is available for accurate determination of the spin moment of a given shell of an uranium atom [17].

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