X-ray magnetic circular dichroism at the U $M_{4,5}$ absorption edges of UFe$_2$

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We present an x-ray magnetic circular dichroism study performed at the U $M_{4,5}$ edges on UFe$_2$, a ferromagnet with almost itinerant $5f$ electrons. The analysis of the branching ratio of the U $M_{4,5}$ edges confirms the fact that the occupation number of the $5f$ states in UFe$_2$ is lower than in other compounds where the f electrons are more localized. Magnetic circular dichroism effects are observed consistently with the presence of an orbital $5f$ magnetic moment which aligns parallel to the total magnetic moment. In agreement with a polarized neutron study, we find a nearly perfect cancellation of the U-$5f$ spin and orbital magnetic moments, which results in a vanishing small total U-$5f$ magnetic moment. Results are discussed in comparison with atomic multiplet calculations. [S0163-1829(97)06505-3]

INTRODUCTION

In these last years actinides and actinide compounds have been the subject of increasing interest due to their very different magnetic behaviors, such as Pauli paramagnetism, localized and itinerant magnetism, and heavy fermions.[1,2] Although f electrons are usually treated as localized, there are some compounds for which the f states are strongly coupled to the conduction band giving rise to unusual properties. Ce and Ce compounds such as CeFe$_2$ are typical examples of this class of materials. This is also the case of actinides and actinide compounds. In fact, the most important parameter responsible for the large variety of magnetic properties of these materials seems to be the delocalization of the U-$5f$ wave functions, intermediate to the case of rare-earth $4f$ and transition metals $3d$ electrons. In intermetallic compounds an essential role in determining the magnetic behavior is also likely to be played by hybridization of the $5f$ orbitals with ligand states.[1]

Even in itinerant f states materials, the spin-orbit coupling can induce important orbital moments[3] if its strength is appreciable compared to the f-band width. Nevertheless, these orbital moments remain smaller than in the atomic case. Since, as a consequence of Hund's third rule, in light actinides the $5f$ spin and orbital magnetic moments are of opposite sign, we might expect the possibility of a net $5f$ spin and orbital moment almost cancelling each other out to give a very small total $5f$ magnetic moment. This is actually the case of UFe$_2$, for which polarized neutron-scattering experiments[2,4,5] have measured a total U-$5f$ magnetic moment $\leq 0.01\mu_B$, with $\mu_L \approx -\mu_S \approx 0.23\mu_B$, in good agreement with theoretical predictions.[6,7]

In this paper we report an x-ray magnetic circular dichroism (XMCD) study at the U $M_{4,5}$ absorption edges of the itinerant ferromagnet UFe$_2$. XMCD is defined as the difference $\sigma^+ - \sigma^-$, σ^+ (σ^-) being the absorption spectrum collected with left (right) circular polarized light. It can be demonstrated that, in the electric dipole approximation, reversing the polarization is equivalent to reversing the magnetization of the sample.[8]

XMCD experiments have been widely performed on the K and $L_{2,3}$ edges of $3d$ transition metals (early experiments

are described in Refs. 9 and 10 respectively), or on $L_{2,3}$ (Refs. 11 and 12) and $M_{4,5}$ (Ref. 13) edges of rare earths. On the contrary, the $M_{4,5}$ edges of actinides have received much less attention. Collins and co-workers have recently measured the XMCD signal in ferromagnetic uranium monosulfide over the U $M_{4,5}$ edges.[14] The observed dichroic signal is larger at correspondence with the M_4 absorption edge and shows the same sign both at the M_4 and at the M_5.

The site and orbital selectivity, typical of absorption spectroscopy, together with the existence of sum rules[15,16] that allows to calculate the ground state, orbital projected $\langle L_z \rangle$ value from the XMCD experimental spectra, make XMCD a powerful instrument to study the magnetic properties of solid-state materials. Even the expectation value for S_z can be evaluated, if a reasonable approximation of the dipolar moment $\langle T_z \rangle$ can be given.[16] Actually, the validity of these sum rules is still an open problem especially for itinerant final states. However, some of us have proved[17] that the $\langle L_z \rangle$ value of the localized $4f$ states of cerium in CeCuSi obtained by the sum rules is in good agreement with the one expected from magnetization experiments. Moreover, band structure calculations[18] and experiments[19] have shown that, in the bulk, the sum rules at the $L_{2,3}$ edges give the good value of $\langle L_z \rangle$ to within 5–10% for the itinerant magnetic systems Fe, Co, and Ni. On the contrary, the sum rule giving $\langle S_z \rangle$ seems affected by larger errors,[16,17] up to 50% for the Ni(001) surface.[20]

We observe magnetic circular dichroism effects in UFe_2, consistently with the presence of orbital $5f$ magnetic moments which align parallel to the total magnetic moment. Our findings confirm the delocalized nature of the $5f$ orbitals and the compensation between $5f$ spin and orbital magnetic moments, which results in a vanishing small U-$5f$ magnetic moment.

EXPERIMENTAL

The polycrystalline UFe_2 compound was prepared by arc-melting stoichiometric amounts of the constituents (U $3N$ and Fe $4N$ pure) in an Ar atmosphere. X-ray diffraction analysis shows a single phase corresponding to the fcc Laves phase with $a_0 = 7.058$ Å. Moreover, ac susceptibility measurements confirm the ferromagnetic state for $T \lesssim 160$ K, with a total magnetic moment $M = 1.16 \mu_B$/formula unit at $T = 20$ K and $B = 2T$.

The XMCD experiments at the U $M_{4,5}$ edges were carried out at the ESRF beamline ID/12A which is dedicated to polarization dependent x-ray absorption studies.[21] The source was the helical indulator HELIOS-II which emits x-ray radiation with a high-polarization rate (above 90%) and flexible polarization (circular left-circular right). The first harmonic of the undulator spectrum was selected to cover the energy range from 3.5 to 3.8 keV. 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 be about 35% at 3.552 keV (M_5 edge) and about 45% at 3.728 keV (M_4 edge). XMCD signals 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 electromagnet. The XANES spectra were recorded at 20 K in the fluorescence detection mode using a Si photodiode associated with a digital lock in exploiting the modulation of the x-ray beam.[22]

In order to extract the absorption signals and to correct for self-absorption effects, the fluorescence spectra were compared (see below) to the data obtained in the sample drain current total electron yield mode on beamline SU22 at the French Synchrotron Radiation Facility (LURE) in Orsay. A double Si(220) crystal monochromator was used to select the wavelength of the radiation emitted by the asymmetric wiggler[23] inserted in the soft x-ray ring Super-ACO.[24] Data were recorded at $T = 50$ K after scraping the sample *in situ* at a base pressure of 1×10^{-9} mbar. The pressure during data acquisition was typically 1×10^{-9} mbar.

RESULTS

Total electron yield (TEY) and fluorescence yield (FY) are indirect methods for measuring absorption cross sections. The first technique detects the number of secondary electrons excited by the decays (mostly Auger) of the core hole created by the absorption of x rays. The electron yield signal is proportional to the absorption cross section of the material[25] as long as the light is absorbed on a length scale significantly longer than the escape depth of the secondary electrons.[26] In the second case the intensity of the light emitted in radiative decays of the core hole is detected. For this reason, FY is essentially bulk sensitive and this is the reason why it has been preferred to TEY in the present experiment. However, in concentrated and thick samples, the fluorescence emission can be strongly reabsorbed resulting in a distortion of the FY spectra.[27] Moreover, even in diluted or thin samples, FY does not measure pure x-ray absorption if atomic multiplet effects are important because, in this case, the fluorescence decay can show a strong dependence on the final state.[28] However, it is important to stress that a recent theoretical investigation finds that the sum rules giving $\langle S_z \rangle$ and $\langle L_z \rangle$ remain, under nonrestrictive assumptions, still valid when applied to FY spectra.[29]

In Fig. 1 the FY spectra are shown as measured. In order to obtain the dichroism spectrum from the fluorescence data, one must correct the FY signals to eliminate self-absorption effects. This can be done in a straightforward way by comparison with the TEY spectrum. A procedure similar to the one used in Ref. 14 is applied. We assume that the M_4 and M_5 fluorescence emission spectra each exhibit a single line whose intensity is considered as a free parameter that is adjusted in order to reproduce the TEY spectrum.[14]

In Fig. 2 we present the corrected FY and the difference spectrum together with the TEY spectrum. The difference is normalized to 100% circular polarization rate. In qualitative agreement with U $M_{4,5}$ XMCD performed on US[14] and on $USb_{0.5}Te_{0.5}$,[30] the dichroic signal is negative at both the M_4 and the M_5 edge (we use opposite sign conventions with respect to Ref. 14 in order to stick to common x-ray-absorption spectroscopy conventions). Another common characteristic is that the dichroic signal presents a well-resolved atomic multiplet structure at correspondence with the M_5 edge, while at the M_4 edge it consists in a broad asymmetric feature. However, the magnitude of the XMCD
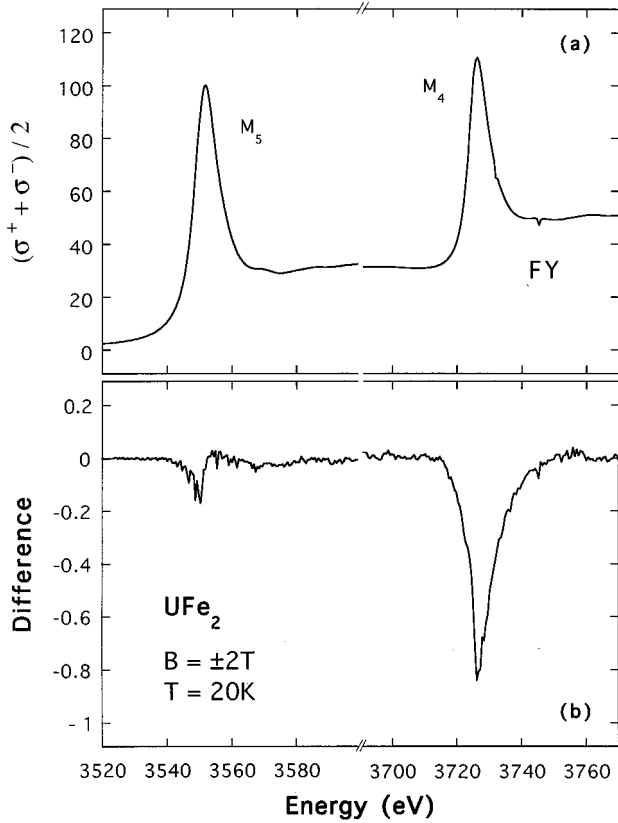
FIG. 1. U $M_{4,5}$ fluorescence yield (FY) of polycrystalline UFe$_2$ obtained at $T=20$ K and under magnetic fields $B=\pm 2$ T. Upper panel: $(\sigma^+ + \sigma^-)/2$; lower panel: $\sigma^+ - \sigma^-$.

FIG. 2. Upper panel: U $M_{4,5}$ total electron yield (TEY) and corrected fluorescence yield (FY) absorption edges of polycrystalline UFe$_2$. Lower panel: XMCD spectrum. The XMCD signal has been normalized to 100% rate of circular light polarization. In the inset are shown atomic pure J multiplet calculation of the U M_5 XMCD spectra convoluted with a Lorentzian function (FWHM=2 eV) to take into account the core hole lifetime broadening: comparison between $5f^3 6d^0 7s^0$ and $5f^2 6d^0 7s^0$ initial states.

spectrum obtained for UFe$_2$ is about 15 times smaller than the one observed for US or USb$_{0.5}$Te$_{0.5}$. This finding is consistent with the expected reduction of the orbital magnetic moment in UFe$_2$ due to the larger delocalization of the $5f$ electrons with respect to the case of US or USb$_{0.5}$Te$_{0.5}$.[5]

According to the sum rules of Refs. 15 and 16, $\langle L_z^{5f} \rangle$ is proportional to the integral of the XMCD intensity across both M_4 and M_5 edges. Within our sign conventions, the negative value of the XMCD signal observed for UFe$_2$ implies that the orbital magnetic moment localized on the U $5f$ electrons aligns *parallel* to the applied magnetic field, i.e., to the *total* magnetic moment, which is essentially due to the spin of the iron $3d$ electrons. This behavior is in good agreement with theoretical predictions[7] and is due to the fact that in UFe$_2$ the hybridization between Fe-$3d$ and U-$5f$ minority spin bands is stronger than between Fe-$3d$ and U-$5f$ majority spin bands. In fact, this leads to antiparallel alignment of the Fe-$3d$ and U-$5f$ spins, in a similar way to what is found in rare-earth intermetallic compounds.[31] Hund's third rule then imposes antiparallel coupling between $5f$ spin and orbital moments, thus leading to the observed parallel alignment between the U-$5f$ orbital and Fe-$3d$ spin moments. Note that this mechanism is independent on the magnitude of L_z and S_z. Since the integral of the XMCD intensity over both edges is proportional to the orbital moment, if $L_z=0$ a nonvanishing dichroic signal should be observed even if the *total* $5f$ magnetic moment is zero, as neutron-diffraction ex-
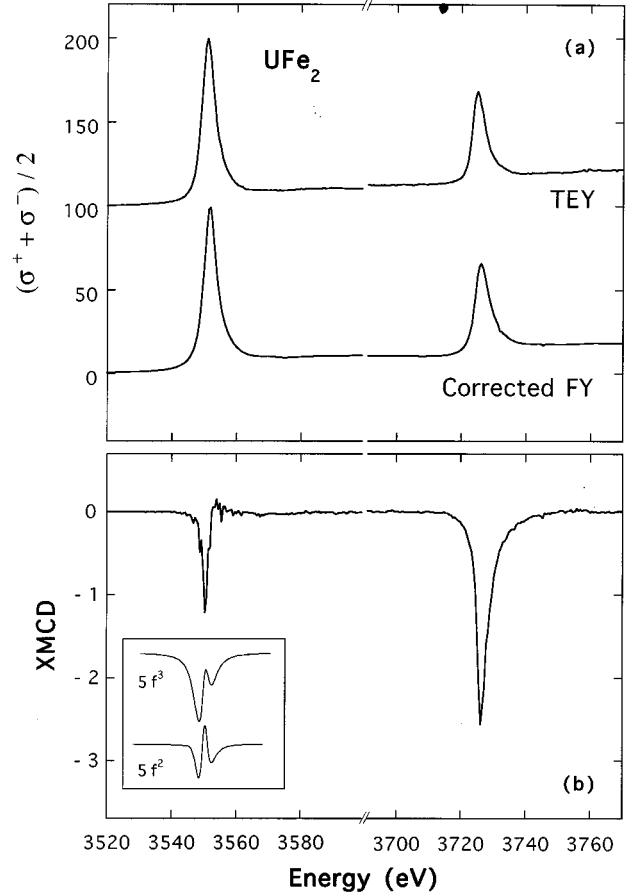
periments and theoretical calculations find in the case of UFe$_2$.[2,4–7]

DISCUSSION

Pure J multiplet calculations give isotropic edges without any resolved multiplet splitting for any value of the occupation number of the $5f$ shell.[32] A general trend consists in the fact that the branching ratio (BR) increases with the number n_{5f} of electrons occupying the f shell. The branching ratio is defined as BR$=I(M_5)/[I(M_4)+I(M_5)]$, where $I(M_4)$ and $I(M_5)$ are the integrated intensities of the M_4 and M_5 isotropic edges. In intermediate coupling its value is BR$=0.67$ for $5f^2$ (corresponding to an U^{4+} ion) and BR$=0.71$ for $5f^3$ (corresponding to U^{3+}).[32] Experimentally, a good approximation of the isotropic spectrum is given by the mean $(\sigma^+ + \sigma^-)/2$ of the spectra collected with opposite circular polarization of the light. The experimental BR is then obtained measuring the areas of the M_4 and M_5 white lines after subtraction of an arctangent function. Its value is 0.70 ± 0.01 for USb$_{0.5}$Te$_{0.5}$ (Ref. 30) while it is only

0.65 ± 0.01 for UFe$_2$. These findings confirm that the occupation number of the $5f$ electrons in USb$_{0.5}$Te$_{0.5}$ is close to $n_{5f}=3$.[5] On the contrary, the isotropic line shape of UFe$_2$ is better described by a configuration in which $n_{5f}=2$. This is coherent with the expected reduction of the $5f$ occupation number due to the strong hybridization of the $5f$ electrons with the valence band which occurs in UFe$_2$.

As for the isotropic absorption edges, no fine structure in the dichroism signal at correspondence with the M_4 edge is predicted by the ionic calculations. On the contrary, the theoretical M_5 XMCD is characterized by a structured line shape which is very sensitive to the occupation number of the $5f$ shell in the ground state.[32] In the inset of Fig. 2 we show a comparison between the atomic multiplet calculations of the M_5 XMCD for an U ion in the $5f^3 6d^0 7s^0$ and in the $5f^2 6d^0 7s^0$ ground-state configuration. The spectra have been convoluted with a Lorentzian function [full width at half maximum (FWHM) $=2$ eV] to account for the core hole lifetime broadening. Apparently, the atomic multiplet calculations fail to reproduce the details of the line shape of the M_5 dichroic signal. This is a proof of the fact that the $5f$ wave functions in UFe$_2$ are not correctly described by an atomic approximation with only pure configurations. The reason should be ascribed to the delocalization of the $5f$ electrons in this system. In order to give a better approximation of the XMCD line shape in UFe$_2$, more detailed calculations are needed, taking into account configuration interactions as well as crystal field effects. Another approach would be the monoelectronic calculation developed by Brooks *et al.* where hybridization is naturally introduced in the formalism.[3,6,7]

For uranium ions $\langle T_z \rangle$ represents a significant contribution to the "effective" $5f$ spin $\langle S_e \rangle = (\langle S_z \rangle + 3\langle T_z \rangle)$, which is the quantity directly determined by applying the spin sum rule.[16] In fact, in intermediate coupling $\langle T_z \rangle / \langle S_z \rangle = 1.16$ and $\langle T_z \rangle / \langle S_z \rangle = 0.62$ for an f^2 and an f^3 ground-state configuration respectively.[32] However, the delocalization of the electrons which takes place in itinerant ferromagnetism can strongly reduce $\langle T_z \rangle$ with respect to its atomic value. Band structure calculations[18] and experiments[19] have shown that, in the bulk, the itinerant magnetic systems Fe, Co, and Ni are characterized by $\langle T_z^{3d} \rangle / \langle S_z^{3d} \rangle \lesssim 0.01$.

By applying the sum rules of Refs. 15 and 16 to the self-absorption corrected XMCD signal of Fig. 2 and supposing that $\langle T_z \rangle = 0$, we find a ratio $\langle L_z \rangle / \langle S_z \rangle$ equal to $-1.95(\pm 5\%)$, which is in excellent agreement with neutron-diffraction results and theoretical predictions.[2,4–7] In order to determine the absolute values of $\langle L_z \rangle$ and $\langle S_z \rangle$, the $5f$ occupation number must be entered in the expression of the sum rules. Taking $n_{5f}=2$ we obtain $\langle L_z \rangle = -0.22\hbar$ and $\langle S_z \rangle = 0.11\hbar$. On the other hand, supposing $n_{5f}=3$ we obtain $\langle L_z \rangle = -0.20\hbar$ and $\langle S_z \rangle = 0.10\hbar$. Thus, we can conclude with some confidence that $\langle L_z \rangle = -0.21 \pm 0.015\hbar$ and $\langle S_z \rangle = 0.10 \pm 0.01\hbar$. The uncertainties on the number of electrons in the $5f$ shell give less than 10% error bars, which are comparable to the intrinsic precision of the sum rules.[16] Once again the values we find are in a very good agreement with the ones of the literature.[2,4–7]

CONCLUSIONS

In conclusion we have performed magnetic circular x-ray dichroism experiments at the U $M_{4,5}$ edges on UFe$_2$, where hybridization effects of the U-$5f$ electrons are important. The analysis of the branching ratio of the U $-M_{4,5}$ edges confirms the fact that the occupation number of the $5f$ states in UFe$_2$ is lower than in other compounds where the f electrons are more localized.

We have found small negative dichroism signals at correspondence with both the U M_4 and U M_5 edges. This observation is consistent with the presence of orbital $5f$ magnetic moments aligned in the direction of the total magnetic moment. The application of the sum rules gives a nearly total cancellation of the spin and orbital magnetic moments leading to a vanishing U-$5f$ total magnetic moment, in good agreement with experimental findings and theoretical predictions. This result is obtained if the expectation value of the dipolar operator T_z is assumed equal to zero.

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