

**X-ray magnetic circular dichroism studies of 5f magnetism in UCoAl and UPtAl**

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Experimental and theoretical x-ray magnetic circular dichroism (XMCD) studies of the intermetallic compounds UCoAl and UPtAl at the uranium  $M_4$  and  $M_5$  edges are reported. UPtAl is a 5f-electron ferromagnet, whereas UCoAl exhibits, at low temperatures and in a magnetic field of 0.65 T, a metamagnetic transition from paramagnetic to ferromagnetic ordering of U moments. Applying the XMCD sum rules to the experimental spectra, expectation values of the orbital and spin magnetic moments of the uranium 5f electrons were calculated. The results show that the orbital-to-spin moment ratio is of comparable value,  $\mu_L/\mu_S \approx -2$ , for both compounds; however, the moments in UCoAl are strongly reduced with respect to UPtAl. Furthermore, the  $\mu_L/\mu_S$  ratio for UCoAl appears to be conserved both in the ferromagnetic and paramagnetic states, although the  $\mu_S$  value in the former case is at least five times larger. The theoretical counterparts of the experimental data were obtained from the electronic structure calculated using the FLAPW method within the local spin density approximation. The calculated x-ray absorption and XMCD spectra show a satisfactory agreement with the experimental data and reproduce well the shape and structure of the spectral lines at the  $M_4$  and  $M_5$  edges.

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**I. INTRODUCTION**

A wide variety of magnetic properties of uranium compounds that reflects various characters of U 5f electrons, ranging from the nearly localized to itinerant, is attracting considerable attention of current condensed matter research. The delocalization of 5f electrons is a consequence of (i) overlaps of the 5f wave functions centered on neighboring U atoms, and (ii) the 5f-ligand hybridization involving uranium 5f states and *s*, *p*, and *d* valence states of ligand atoms.<sup>1</sup> The two mechanisms play a dual role in magnetism. They cause a delocalization of 5f electrons and a consequent washout of U magnetic moments; however, on the other hand, they mediate strong exchange interactions between U moments. The magnetic behavior of a particular material is a result of the interplay of these two effects that is closely connected with interatomic distances, U-atom coordination, and the nature of ligands. The itinerant character of electron states usually implies a strong reduction of the orbital magnetic moment with respect to the free-atom expectation value. Nevertheless, in contrast to 3d electrons in transition metals, sizable orbital magnetic moments are observed in U intermetallic compounds with apparently strongly delocalized 5f electrons, e.g., in UNi<sub>2</sub>.<sup>2,3</sup> It is the very strong spin-

orbit coupling present in actinides that also induces an orbital moment in the case of itinerant 5f-electron states. Analyzing spin and orbital magnetic moments in various actinide compounds, Lander *et al.* suggested that the ratio of the orbital to the spin moments provides information on the strength of 5f-ligand hybridization, and consequently the delocalization of involved 5f electrons.<sup>4</sup> The individual values of orbital and spin components, however, bear essential information, and therefore relevant experiments and first-principles electronic structure calculations become an important issue of 5f-electron compounds.

The x-ray magnetic circular dichroism (XMCD) technique developed in recent years evolved into a powerful magnetometry tool to separate orbital and spin contributions to magnetic moments. It is an element specific method, which explores magnetism of electrons in a specific shell of a particular atom. The quantitative nature of XMCD techniques is based on a sum rule analysis of spin-orbit split spectra of core levels, e.g.,  $M_4$  and  $M_5$  edges of uranium.<sup>5,6</sup>

In this paper we concentrate on two ternary uranium intermetallic compounds, an itinerant 5f-electron metamagnet UCoAl and a ferromagnet UPtAl. Both compounds crystallize in the hexagonal ZrNiAl-type structure, and exhibit a huge magnetocrystalline anisotropy as well as a number of

UTX counterparts ( $T$  is a transition metal,  $X$  is a  $p$ -electron metal). This structure has a layered character and consists of alternate  $U$ - $T(1)$  and  $T(2)$ - $X$  basal plane layers.<sup>7</sup> Uranium atoms occupy one equivalent position, and the transition metal atoms possess two crystallographically nonequivalent positions in the two layers with an occupancy ratio  $T(1):T(2) = 1:2$ . The interatomic distances between uranium ions in UCoAl and UPtAl compounds are 0.349 and 0.360 nm respectively, which is in the range of Hill limit.<sup>7</sup>

UCoAl is very interesting system that shows no magnetic ordering down to the lowest temperatures, but in a relatively low magnetic field applied along the  $c$  axis a metamagnetic transition to a ferromagnetic state is observed at low temperatures. The metamagnetic transition in UCoAl is attributed to the band metamagnetism observed, e.g. in YCo<sub>2</sub>.<sup>9</sup> In contrast to the almost isotropic metamagnetic behavior of YCo<sub>2</sub>, in UCoAl, we observe a huge uniaxial anisotropy. The metamagnetism is induced only when the magnetic field is applied along the  $c$  axis, whereas in fields in a perpendicular direction UCoAl behaves like a Pauli paramagnet and no metamagnetic transition is observed in magnetic fields up to 42 T.<sup>10</sup> The strong uniaxial magnetic anisotropy is preserved in both compounds UPtAl and UCoAl, at least up to room temperature. It is of interest to characterize a rather low ordered magnetic moment of UCoAl which amounts  $0.30\mu_B/\text{f.u.}$  (at 4.2 K) above the metamagnetic transition. The moment steadily increases with magnetic field, showing no saturation tendency up to 35 T where it reaches the value of  $0.6\mu_B/\text{f.u.}$ <sup>10,11</sup>

The UPtAl compound is an appropriate reference system for a more localized compound of the same structure and with composition and bonding similar to that of UCoAl. It orders ferromagnetically below  $T_C = 43$  K with a saturated magnetization of  $1.38\mu_B$  per formula unit at 2 K in fields applied along the  $c$  axis.<sup>8</sup> The strong uniaxial anisotropy is manifested by the fact that the magnetization measured along the  $a$  axis is much smaller and has no spontaneous component (in fact, it resembles a magnetic response of a paramagnet exhibiting  $0.28\mu_B/\text{f.u.}$  at 40 T).

The fundamental issue of the experiment reported here concerns the mechanism of the metamagnetic transition in UCoAl, and the field-induced development of its orbital and spin moments. In connection with this it is also important to investigate the role of orbital magnetism, since it has recently been realized that delocalized band states may sometimes carry an appreciable orbital moment. For this purpose we have studied XMCD at the uranium  $M_4$  and  $M_5$  edges. This technique makes it possible to extract values of the orbital and effective spin component of the magnetic moment on uranium atoms; this along with the electronic structure calculations presented in this paper, will contribute to our understanding of this interesting system.

## II. EXPERIMENTAL DETAILS

The XMCD measurements were carried out at the ESRF in Grenoble on the beamline ID12A that is dedicated to the polarization-dependent x-ray absorption fine structure studies.<sup>12</sup> A helical electromagnetic undulator Helios-II, pro-

vided a high flux of photons of tunable helicity with high degree of circular polarization close to 1. Due to the reflections on focusing optics and on a monochromator, the polarization degree of the incident beam was reduced to  $P \approx 0.45$  at the  $M_4$  edge and  $P \approx 0.35$  at the  $M_5$  edge. The required photon energy was selected by a cooled Si crystal (111) double monochromator, which has a typical spectral resolution of 0.5 eV in the spectral range 3.5–3.8 keV. The studied bulk samples are not transparent for x rays so that the x-ray absorption spectra were recorded by monitoring the total fluorescence yield (FY).

The XMCD signal was obtained from the FY spectra at  $M_4$  and  $M_5$  edges by consecutively reversing both the helicity of the beam and the polarity of the magnetic field. In order to eliminate the effects connected with circular dichroism of a nonmagnetic origin and different polarization degrees for right- and left-hand polarized beams, each spectrum was measured four times—at either polarity of the magnetic field the spectra for right and left helicities were scanned. Appropriate processing of these four spectra made it possible to reduce these contributions to a minimum. The temporal changes of the FY signal (originating, e.g., from small temporal fluctuations of the beam polarization, beam position, and the stability of electromagnetic undulator) were eliminated by accumulation of sufficient data. In this way it was possible to achieve relative signal accuracy of  $10^{-4}$ .

In order to extract the absorption and dichroism from the fluorescence spectra several corrections of the experimental data had to be done. The self-absorption (i.e. the absorption of the secondary photons in the sample) is the most important effect that leads to a “saturation” of the optical signal, resulting in distortion of the fluorescence spectral lines especially in the vicinity of the absorption edge. The self-absorption can be taken into account in a straightforward way by comparing the fluorescence signal with isotropic spectra measured in the electron yield detection. For these reasons we also measured the total electron yield (TEY) spectra of UCoAl sample over the  $M_4$  and  $M_5$  edges by sample current measurements. Such corrections for saturation effects are relatively simple and straightforward, and provide reliable results. Provided that the fluorescence is corrected for the self-absorption, it can be considered with confidence as a measure of the uranium absorption.<sup>13,14</sup> Comparing various uranium compounds, all the TEY spectra show a similar shape with a comparable white line peak to edge jump ratios.<sup>13,15</sup> The corrections of UPtAl spectra were made in a similar way as those for UCoAl. The resultant XMCD spectra were subsequently corrected for the polarization degree of the incident beam. It is worth noting that the numerical values of the magnetic moments calculated using the sum rules only little depend (of the order of  $\pm 5\%$ ) on performed corrections of the FY signal, and the ratio  $\mu_L/\mu_S$  especially is almost uninfluenced by these corrections.

High quality single crystals of UCoAl and UPtAl were studied in this experiment. The magnetic and structure properties of samples cut from the same single crystals were reported elsewhere.<sup>8,10,16</sup> The experiment was carried out for temperatures and magnetic fields where these two compounds exhibit magnetic ordering. In particular, temperature

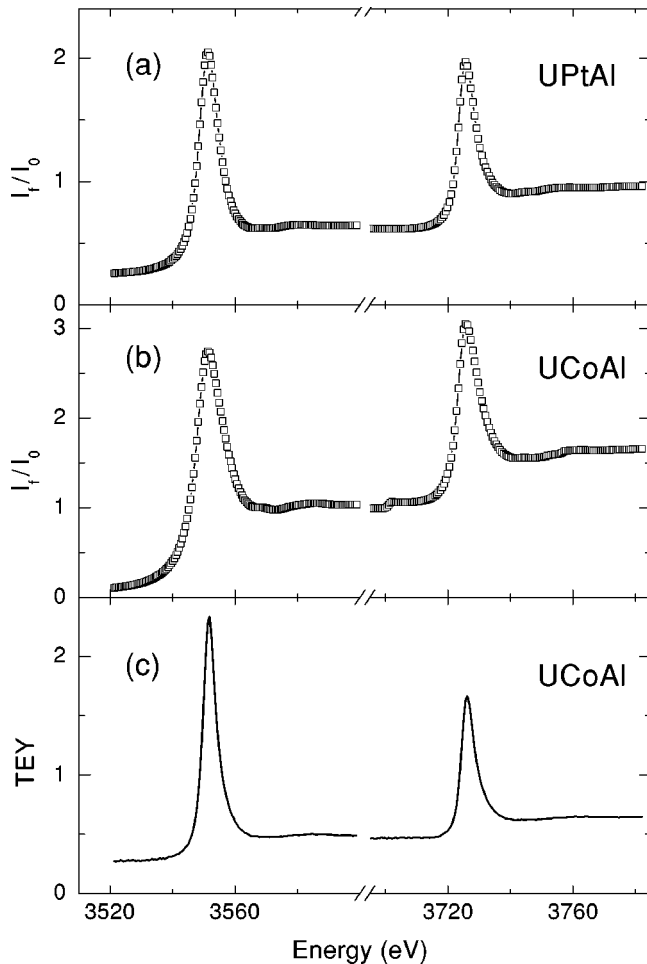


FIG. 1. Total fluorescence yield spectra of UPtAl (a) and UCoAl (b) and isotropic total electron yield (TEY) spectra of UCoAl (c) at the uranium  $M_4$  and  $M_5$  absorption edges. The fluorescence spectra were measured at 10 K, and the TEY spectrum of UCoAl was measured at a room temperature.

was fixed at  $T=10$  K for both samples. UCoAl was measured in magnetic fields in the range from 0.7 up to 7 T whereas a field of 2 T was applied in case of UPtAl to saturate the sample. The measurements were made in the Faraday configuration where both incident beam and magnetic field were parallel (oriented along the  $c$  axis) and normal to the sample surface.

### III. RESULTS AND DISCUSSION

The x-ray absorption measurements were performed through the uranium  $M_4$  and  $M_5$  edges. These edges correspond to electronic transitions from the uranium core  $3d$  states to the  $5f$  band states. The total fluorescence and total electron yield spectra are displayed in Fig. 1. The self-absorption effects resulting in decreased intensities of the fluorescence peaks are clearly observed in Fig. 1. The corrected x-ray absorption and corresponding dichroism spectra of UCoAl are presented in Fig. 2. Since the differences in absorption for particular beam helicities and/or opposite magnetic fields are very small in this sample, the curves

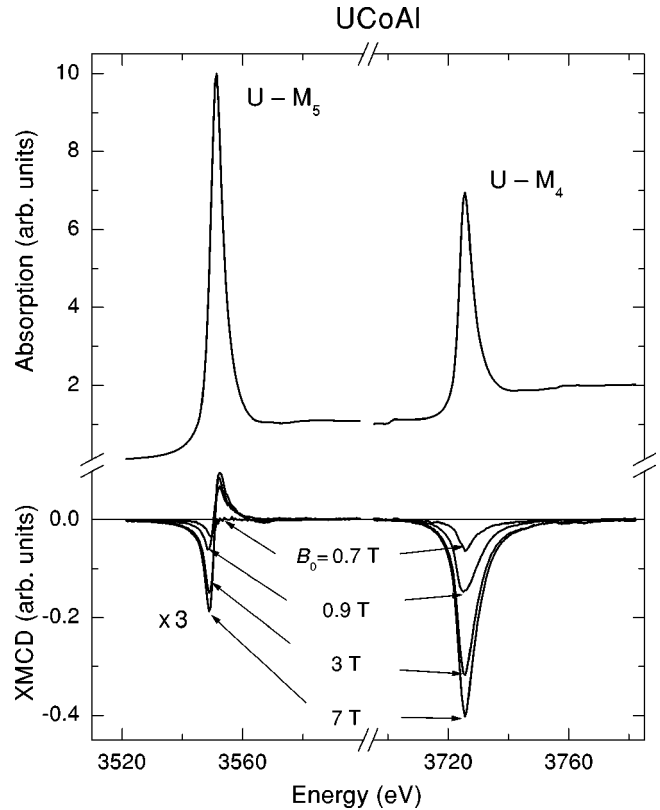


FIG. 2. X-ray absorption (a) and XMCD (b) spectra of UCoAl single crystal at the uranium  $M_4$  and  $M_5$  edges as a function of magnetic field. The measurements were made at  $T=10$  K, and the beam direction and magnetization were oriented along the  $c$  axis. The spectra were deduced from the fluorescence signal (Fig. 1) corrected for self-absorption. The displayed XMCD curves correspond to the difference in absorption coefficients,  $\Delta\alpha = \alpha^+ - \alpha^-$ , corrected for the degree of circular polarization of the incident beam, see text for details.

almost coincide and cannot be distinguished in the plot. The spectra taken in 3 and 7 T correspond to the ferromagnetic state. At 0.7 T the paramagnetic state predominates and ferromagnetic ordering starts to develop above this field. The absorption and XMCD spectra of the ferromagnetic UPtAl measured under the magnetic saturation are shown in Fig. 3. The XMCD signal of UPtAl is much higher compared to that of UCoAl, and the absorption lines for opposite helicities are clearly observed at the  $M_4$  edge. The dichroic  $M_4$  line consists of a single nearly symmetric negative peak. Such a peak is characteristic at the  $M_4$  edge of all uranium systems. The spectral shape at the  $M_5$  edge is more complex. In both UPtAl and UCoAl (above the metamagnetic transition) the dichroic line at the  $M_5$  edge has an asymmetric  $s$  shape with two peaks—a stronger negative peak and a weaker positive peak. The different shape of the dichroic  $M_5$  line measured at a low field of 0.7 T, where the positive peak is not developed, may be questioned due to the small signal-to-noise ratio of measurements in the paramagnetic region of UCoAl. In subsequent sections we compare our findings resulting from applying the sum rules to the spectra with the data obtained from neutron scattering and first-principles calculations.

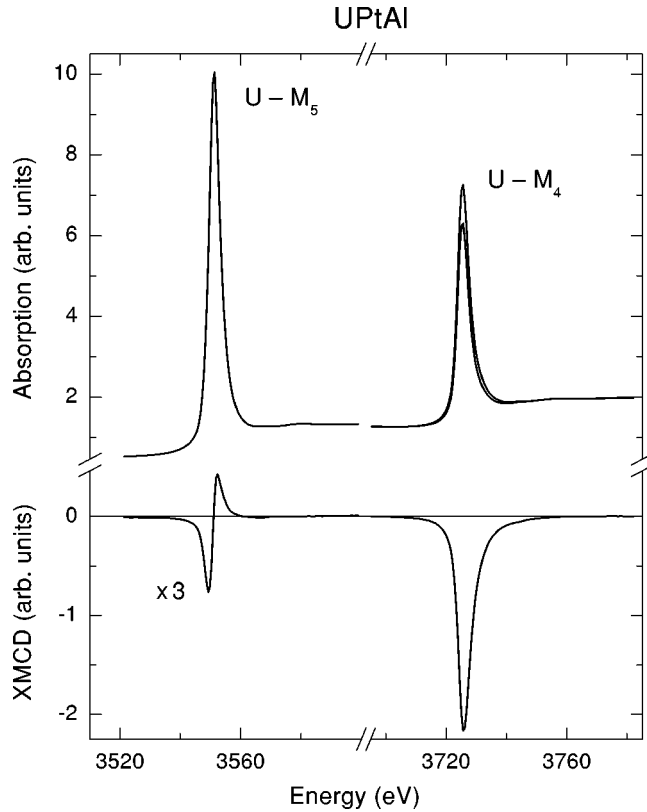


FIG. 3. Uranium  $M_4$  and  $M_5$  absorption spectra for opposite field polarity (a) and XMCD spectra (b) of a UPtAl single crystal measured along the  $c$  axis at  $T=10$  K. The measurements were made under  $B_0=2$  T corresponding to the magnetic saturation. The spectra were corrected for self-absorption and polarization degree in a similar way as those for UCoAl (Fig. 2).

#### A. XMCD, orbital, and spin moments

The properties of  $5f$  electrons are conveniently probed in x-ray absorption experiments by excitation of  $3d$  core electrons to unfilled  $5f$  states. The absorption spectra are characterized by strong resonances near  $M_4$  ( $d_{3/2}$ ) and  $M_5$  ( $d_{5/2}$ ) edges, so called white lines. The use of circularly polarized x rays opens the door for x-ray based spectroscopy studies of magnetic materials and structures.<sup>17,18</sup> The right- (RCP) and left-hand circularly polarized (LCP) photons preferably generate spin-up and spin-down photoelectrons, respectively, and the difference in the transition intensities reflects the difference in the spin-up and spin-down holes of the  $f$  shell. In this process the RCP and LCP photons transfer their angular momentum to the excited photoelectron which carries the transferred momentum as a spin or orbital moment, or both. Since  $d_{5/2}$  and  $d_{3/2}$  levels have opposite spin-orbit couplings the spin polarization is opposite at these two edges. The spin-split valence shell acts as a detector for the spin of an excited photoelectron. Similarly, if the  $f$  valence shell possesses an orbital moment it acts as an orbital momentum detector for excited photoelectron.

The difference in absorption coefficients for RCP and LCP photons, i.e., photons with opposite helicities, results in nonzero XMCD. The XMCD has several capabilities that are not afforded by traditional magnetic analysis techniques. Its

foremost strength is the element-specific quantitative determination of spin and orbital magnetic moments and their anisotropies.

The core  $d$  levels of uranium atoms are spin orbit split into well-defined sublevels. The absorption signals of corresponding electron transitions at  $M_4$  and  $M_5$  edges are proportional to the number of holes in the final uranium  $5f_{5/2}$  and  $5f_{7/2}$  states, respectively. That is, the signal at the  $M_4$  edge originates from the electric dipole transitions  $3d_{3/2} \rightarrow 5f_{5/2}$  and that at the  $M_5$  edge originates primarily from  $3d_{5/2} \rightarrow 5f_{7/2}$  transitions, with a weaker contribution from  $3d_{5/2} \rightarrow 5f_{5/2}$  transitions. Since the  $5f_{7/2}$  band is only slightly populated and most  $f$  electrons fill the  $5f_{5/2}$  band, only the latter band exhibits significant magnetic moment.

The quantitative nature of the XMCD technique is based on a sum rule analysis of experimental XMCD and absorption spectra. These rules derived by Carra and co-workers,<sup>5,6</sup> correlate the ground state orbital and effective spin moment operators  $\langle L_z \rangle$  and  $\langle S_e \rangle$ , respectively, to the integrated dichroism signal over pairs of spin-orbit-split core-level excitations. The sum rules for XMCD spectra at the uranium  $M_{4,5}$  edges, involving  $3d \rightarrow 5f$  transitions, read<sup>5,19</sup>

$$\langle L_z \rangle = \frac{3n_h \int_{M_5+M_4} \Delta\alpha(E) dE}{\int_{M_5+M_4} (\alpha^+(E) + \alpha^-(E) + \alpha^{iso}(E)) dE}, \quad (1)$$

$$\langle S_e \rangle = \frac{3n_h}{4} \frac{2 \int_{M_5} \Delta\alpha(E) dE - 3 \int_{M_4} \Delta\alpha(E) dE}{\int_{M_5+M_4} (\alpha^+(E) + \alpha^-(E) + \alpha^{iso}(E)) dE}, \quad (2)$$

where  $\alpha^\pm$  are the absorption coefficients for opposite beam helicities related to the  $M_{4,5}$  edges;  $\Delta\alpha = \alpha^+ - \alpha^-$  corresponds to the dichroism;  $\alpha^{iso}$  is the isotropic absorption, which can be presumed here to be  $\alpha^{iso} = (\alpha^+ + \alpha^-)/2$  with good accuracy;  $n_h = (14 - n_f)$  is the number of holes in the  $5f$  shell and  $n_f$  the number of  $5f$  electrons;  $E = \hbar\omega$  is the photon energy. The effective spin operator  $\langle S_e \rangle$ , is related to the spin moment operator  $\langle S_z \rangle$  and for  $5f$  electrons we have<sup>5</sup>

$$\langle S_e \rangle = \langle S_z \rangle + 3\langle T_z \rangle, \quad (3)$$

where  $\langle T_z \rangle$  is the magnetic dipole operator that correlates spin moments with their positions and  $z$  is the quantization axis (parallel to the crystallographic  $c$  axis). In spite of the limited applicability of the sum rules to solids, since they were derived based on a strict atomic approach, the results obtained for number of  $3d$  and  $5f$  compounds appeared to be in surprisingly good agreement with other methods.

Numerical integration of the XMCD and absorption spectral curves (Figs. 2 and 3), over the  $M_{4,5}$  edges, using Eqs. (1) and (2), allow one to extract ground state expectation values of the orbital and effective spin moments of a probed uranium  $5f$  shell. In these calculations the absorption curves were corrected for the background absorption by a steplike

TABLE I. Uranium  $5f$  magnetic moments of UCoAl and UPtAl deduced from the XMCD spectra. The values of UCoAl for different fields  $B_0$  are shown, UPtAl data correspond to the magnetic saturation. The orbital  $\mu_L$  and spin  $\mu_S$  moments were calculated for two possible electron configurations using theoretical values of the dipolar term  $\langle T_z \rangle$ ; see the text for details. Moments are expressed in  $\mu_B$ .

	$B_0$ [T]	$\mu_L$		$\langle L_z \rangle / 2 \langle S_z \rangle$	$-\mu_S$		$-\mu_L / \mu_S$	
		$5f^2$	$5f^3$		$5f^2$	$5f^3$	$5f^2$	$5f^3$
UCoAl	0.7	0.090	0.082	-0.76	0.026	0.040	3.45	2.05
	0.9	0.22	0.20	-0.64	0.075	0.115	2.90	1.75
	1	0.24	0.22	-0.61	0.09	0.13	2.70	1.65
	3	0.45	0.41	-0.71	0.14	0.22	3.15	1.90
	7	0.54	0.49	-0.71	0.17	0.25	3.16	1.95
UPtAl	2	2.49	2.28	-0.71	0.79	1.19	3.15	1.92

function. Since the sum rules involve only the integrated intensity of the spectra, the results are independent on the detailed shape of spectral lines. Combining Eqs. (1) and (2) we see that the integrated XMCD signal over either the  $M_4$  or  $M_5$  line is proportional, respectively, to  $\langle L_z \rangle - 2 \langle S_z \rangle$  or  $\langle L_z \rangle + 4 \langle S_z \rangle / 3$ . Due to opposite signs of  $\langle L_z \rangle$  and  $\langle S_z \rangle$  operators in light actinides, much stronger dichroism is expected at the  $M_4$  edge than at the  $M_5$  edge. This is in agreement with microscopic considerations taking into account different populations of the  $f_{5/2}$  and  $f_{7/2}$  subbands discussed in the next sections.

According to Eqs. (1) and (2) the calculated values of  $\langle L_z \rangle$  and  $\langle S_z \rangle$  are dependent on the uranium atom valence, which is, however, unknown due to the strong  $5f$ -ligand hybridization. The performed first-principles calculations of the electronic structure provide the  $5f$  occupancy number  $n_f \approx 2.46$  for UCoAl, i.e., a value close to an average between the  $5f^2(\text{U}^{4+})$  and  $5f^3(\text{U}^{3+})$  configurations.<sup>20</sup> The occupancy number does not change much in the ternary UTAI compounds. Nevertheless, the choice of  $n_h$  in Eqs. (1) and (2) is not critical, and the inaccuracy introduced in the value of the orbital moment  $\mu_L$  is not greater than  $\pm 4\%$  as long as  $n_h \gg n_f$ .

On the other hand, the spin magnetic moment  $\mu_S$  is retrieved with a higher relative error. The main difficulty in evaluating  $\mu_S$  arises from the determination of the dipolar operator  $\langle T_z \rangle$ . In itinerant magnetic systems the dipolar term is usually very small, and for  $3d$  metals it proved to be negligible.<sup>21,22</sup> However, in  $5f$ -electron compounds the dipolar term  $\langle T_z \rangle$  forms a substantial contribution comparable to the spin term  $\langle S_z \rangle$ , and it cannot be neglected. There is no straightforward way to determine its value with a sufficient accuracy. Nevertheless,  $\langle T_z \rangle$  can be estimated either from theoretical considerations or combined XMCD and neutron diffraction experiments. Based on intermediate spin-orbit coupling scheme, van der Laan and Thole<sup>23</sup> found, for free ions, ratios of the magnetic dipole to the spin moment on  $R_T = \langle T_z \rangle / \langle S_z \rangle = 1.15$  and  $0.57$  for respective  $5f^2$  and  $5f^3$  configurations.

Therefore, two approaches are employed and compared in this work. First, the moments are evaluated using Eqs. (1)–(3) for both configurations,  $n_f = 2$  and  $3$ , where the spin moment  $\mu_S$  is calculated using theoretical values of  $R_T$ . Sec-

ond, the spin moment is computed by combining the XMCD-deduced value of the orbital moment [Eq. (1)], and the total uranium magnetic moment obtained from diffraction of polarized neutrons.

## B. UCoAl

The results of numerical integration of the spectra are listed in Table I. In these calculations theoretical values of  $R_T$  for  $5f^2$  and  $5f^3$  configurations were adopted. The orbital and spin moments reported in the table are respectively defined as  $\mu_L = -\langle L_z \rangle \mu_B$  and  $\mu_S = -2 \langle S_z \rangle \mu_B$ , where  $\mu_B$  is the Bohr magneton. Notice that the ratio  $\langle L_z \rangle / \langle S_z \rangle$  does not depend on the number of  $5f$  electrons, and its value is determined exclusively by the dichroic spectra. We see from the Table I that this ratio changes much below and above the metamagnetic transition of UCoAl, and is almost the same as in UPtAl. While the orbital moments  $\mu_L$  are obtained with reasonable accuracy for both tested configurations, the calculated spin moments  $\mu_S$  strongly depend on the chosen value of  $n_h$ . In addition, the orbital-to-spin-moment ratio  $\mu_L / \mu_S$  is rather high, especially for the  $5f^2$  configuration. These results indicate that the  $5f^2$  configuration is rather unrealistic, and the values of  $\mu_S$  presented in Table I should be interpreted with caution.

The spin moments calculated by the second approach (combining the XMCD values of  $\mu_L$  and the total uranium magnetic moment  $\mu_U$  obtained from neutron diffraction data) are summarized in Table II. Since experimental neutron

TABLE II. Parameters of UCoAl and UPtAl calculated by combining the XMCD data and the total uranium moment  $\mu_U$  estimated from neutron diffraction and magnetization studies. Displayed orbital moments  $\mu_L$  correspond to the intermediate  $5f$  occupancy,  $n_f = 2.5$ . Experimental values of  $R_T$  were obtained from  $R_T = (\langle S_z \rangle - \langle T_z \rangle) / 3 \langle S_z \rangle$ . The numbers in parentheses are experimental errors representing limiting values for  $n_f = 2$  and  $3$ . Moments are expressed in  $\mu_B$ .

	$B_0$ [T]	$\mu_L$	$-\mu_S$	$-\mu_L / \mu_S$	$R_T$	$\mu_U$
UCoAl	7	0.52(2)	0.17(2)	3.06(30)	1.10(13)	0.35
UPtAl	2	2.39(10)	1.14(10)	2.10(10)	0.65(5)	1.25

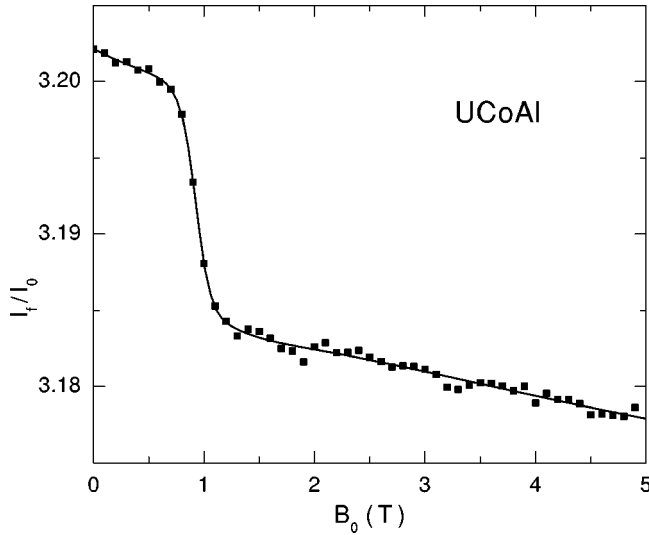


FIG. 4. Magnetic field dependence of the total fluorescence yield measured at the maximum of the  $M_4$  edge at  $T=10$  K. The solid line is a guide for the eye.

data are not available exactly for the magnetic fields and temperatures used in our experiment, the total uranium magnetic moment  $\mu_U$  of UCoAl was estimated from measurements performed at 2 and 5 K.<sup>11,16</sup> Extrapolation of the neutron data leads to  $\mu_U=0.35\pm 0.02\mu_B/U$  for an external magnetic field of 7 T and a temperature of 10 K. Obviously, the spin moment calculated in this way (see Table II), is rather small. This consequently leads to an unrealistically high  $\mu_L/\mu_S$  ratio. Likewise the computed ratio  $R_T$  is far from theoretical values. Although our values of  $\mu_S$  and  $\mu_L$  are in good agreement with neutron data reported by Wulff *et al.*,<sup>11</sup> the latest polarized neutron studies performed by Javorsky *et al.*,<sup>16</sup> on a sample cut from the same single crystal as we have used for XMCD, provided fairly higher values of  $0.78\mu_B$  for the orbital and  $-0.38\mu_B$  for the spin moment (at  $T=2$  K and  $B_0=8$  T).

These facts suggest that the orbital, and consequently also the spin moments, deduced using the sum rules are underestimated (even though taking into account the higher temperature of XMCD measurements of UCoAl compared to neutron diffraction experiments). There are two reasons for such observations. First, the underestimation of  $\mu_L$  is suspected to be an inherent property of the XMCD sum rules. Compared to neutron data the XMCD-derived orbital moments in a number of uranium samples are generally smaller.<sup>24</sup> Another problem, particularly important in metamagnetic systems like UCoAl, applies to the quality of sample surface probed by x rays. Unfortunately, most of intermetallic samples cannot be cleaved, and thus the sample surface has to be mechanically polished. Such a process may result in a degradation of the sample surface layer to a certain extent, and thus some reduction of the total magnetic moment in the surface layer is suspected. Nonetheless, in our UCoAl sample we have observed a well-resolved metamagnetic transition in the x-ray fluorescence signal (Fig. 4) and thus the surface degradation is not crucial.

Let us now turn to the spin and orbital components of UCoAl obtained at different magnetic fields. As mentioned above, the magnetic moment does not saturate above the metamagnetic transition and steadily increases. According to Eq. (1) the orbital moment is proportional to the sum of areas below the  $M_4$  and  $M_5$  spectral lines in the XMCD spectrum. We see in Fig. 2 that the intensities of both lines increase with increasing magnetic field. As a consequence both orbital and spin components increase, and they develop in a similar way with the field; see Table I for numerical values. The ratio  $\mu_L/\mu_S$  is roughly independent of the external field, and it adopts comparable values in all the field ranges both for paramagnetic and ferromagnetic states of UCoAl.

In conclusion of this section, the results confirmed that magnetism in UCoAl is undoubtedly dominated by the orbital component, which is larger and antiparallel to the spin moment. In addition, both  $\mu_L$  and  $\mu_S$  are strongly reduced in UCoAl with respect to the corresponding free ion values. However, the ratio of orbital-to-spin moment,  $\mu_L/\mu_S$ , estimated from our data is rather high and is close to  $-2$  for the presumed  $5f^3$  configuration. We remind that the free ion values of this ratio within the intermediate coupling scheme are  $-3.42$  and  $-2.57$ , respectively, for  $5f^2$  and  $5f^3$  configurations. In spite of the higher relative error coming mostly from the uncertainty in the uranium valency, the ratio  $\mu_L/\mu_S$  remains fairly high, and the orbital moment compared to the spin moment is sizable.

### C. UPtAl

The ferromagnetic UPtAl exhibits a large dichroic signal and the components for opposite helicities or opposite magnetic fields are well resolved in the spectra, as can be seen in Fig. 3. The orbital and spin moments of UPtAl were calculated in a similar way as in case of UCoAl. Table I contains moments obtained for both the  $5f^2$  and  $5f^3$  configurations adopting theoretical values of  $R_T$ . The calculated uranium orbital moment of UPtAl,  $\mu_L\approx 2.4\mu_B$ , is much higher in comparison to UCoAl. The spin moments are  $\mu_S=0.8\mu_B$  and  $1.2\mu_B$ , and the ratios  $\mu_L/\mu_S=-3.1$  and  $-1.9$  for respective  $5f^2$  and  $5f^3$  configurations. Again, the  $5f^2$  configuration provides unrealistic values.

The spin moments obtained by combining the XMCD-deduced orbital moment and the total uranium moment provided by the magnetization measurements are presented in Table II. To our knowledge no reliable polarized neutron scattering data are available for this compound. Taking into account that the Pt polarization is quite small (cf. Table III), the total uranium magnetic moment in UPtAl at 10 K was estimated  $\mu_U\approx 1.25\mu_B/U$  (the saturated moment at 4.2 K is  $\mu_{sat}=1.38\mu_B/U$ ). As a result for the spin moment we receive  $\mu_S\approx 1.14\mu_B$ , and for the ratio  $\mu_L/\mu_S\approx -2.1$ . These values are in close correspondence with those estimated above for the  $5f^3$  configuration. The value of the dipole operator ratio calculated from these data,  $R_T=0.65$ , also favors the  $5f^3$  electron configuration.

We can conclude that magnetism of UPtAl is dominated by the orbital component, which is larger and antiparallel to the spin moment. Both  $\mu_L$  and  $\mu_S$  components are much

TABLE III. The spin  $\mu_S$  and orbital  $\mu_L$  moments of the individual atoms in UAl compounds as calculated by the FLAPW method.  $T(1)$  and  $T(2)$  represent the transition metals Co, Pt, or Rh situated in U- $T(1)$  or Al- $T(2)$  layers, respectively. Moments are expressed in  $\mu_B$ .

	UCoAl		UPtAl		URhAl	
	$\mu_L$	$\mu_S$	$\mu_L$	$\mu_S$	$\mu_L$	$\mu_S$
U	1.19	-1.01	2.06	-1.63	1.59	-1.22
$T(1)$	0.01	0.12	-0.01	0.02	-0.01	0.05
$T(2)$	0.03	0.17	-0.02	0.03	0.01	0.07

higher than those in UCoAl. The rather high value of the  $\mu_L/\mu_S$  ratio suggests a moderate reduction of the orbital moment compared to its free ion value.

#### D. First-principles calculations

The magnetic moments, x-ray absorption, and XMCD spectra at the uranium  $M_{4,5}$  edges were obtained from the electronic structure calculated using the local spin density approximation (LSDA) to the density functional theory. In particular, the WIEN97 implementation of the full-potential linearized augmented-plane-wave (FLAPW) method was used.<sup>25</sup> The basis set for expansion of the wave functions consisted of approximately 1260 LAPW functions, including uranium 6s and 6p, cobalt 3p, and aluminum 2p local orbitals. The calculation was performed on a regular mesh consisting of 105  $k$  points in the irreducible wedge of the Brillouin zone. Careful tests with respect to  $k$  points were made, and we have found that our values of magnetic moments converged reliably. The spin-orbit coupling was included by the standard second variational-step method. The cutoff energy for the second variational step was approximately 50 eV above the Fermi energy.

The quasiparticle functions and energies were approximated with the Kohn-Sham eigenfunctions and eigenenergies for the purpose of calculation of the XMCD and x-ray absorption spectra. The relaxation effects, resulting in a smearing of the spectra, were simulated by combined Lorentzian and Gaussian artificial broadenings adjusted by comparison to the experiment. The absolute value of the  $M_5$  absorption threshold was adjusted by comparison to the experiment, while the  $M_5$ - $M_4$  splitting was obtained by a solution of the Dirac equation in the spherical part of the spin-averaged self-consistent crystal potential. This splitting is determined mainly by the energy separation of  $3d_{5/2}$  and  $3d_{7/2}$  levels, and does not depend on any adjustable parameter.

The self-consistent spin-polarized calculation converged to ferromagnetic ground state, for both studied systems. The resulting spin and orbital moments are shown in Table III. With respect to the experimental fact that UCoAl has a paramagnetic ground state we note that we did not intend to study the actual ground state by total energy calculations. This would have required a search for equilibrium lattice constants  $a$  and  $c$  and positional parameters  $x_U$ ,  $z_U$ ,  $x_{Al}$ , and  $z_{Al}$ . We used experimental lattice parameters instead, and assumed that the calculated ferromagnetic state can serve

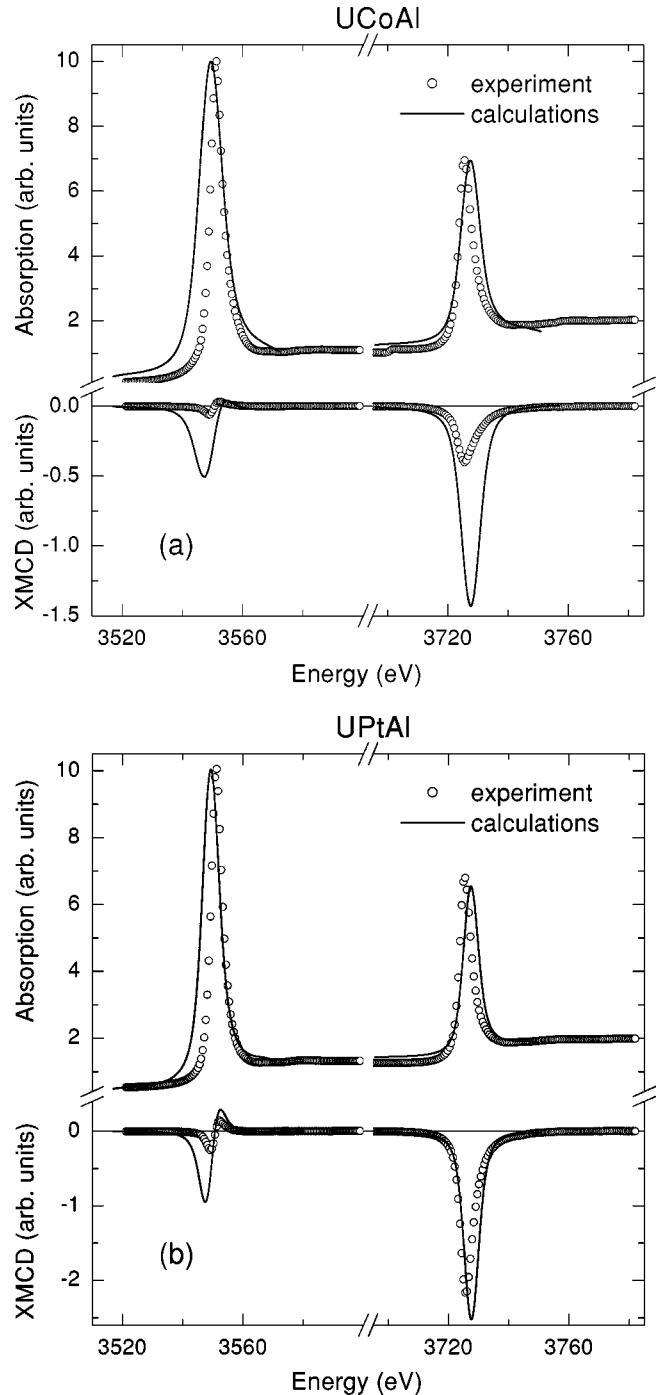


FIG. 5. Isotropic absorption and XMCD spectra of UCoAl (a) and UPtAl (b) at the uranium  $M_{4,5}$  edges calculated from the first principles (solid lines). Experimental spectra (symbols) were measured at 10 K and at magnetic field 7 T for UCoAl and 2 T for UPtAl, respectively. The spectra were scaled so that they exhibit the same intensity at the  $M_5$  peak.

as an approximate description of UCoAl above the metamagnetic transition. In Fig. 5 we show the calculated x-ray absorption and XMCD spectra together with experimental data. Larger amplitude of the calculated XMCD spectra of UCoAl corresponds to larger theoretical moments as compared to the experimental ones. This result is somewhat unusual for ura-

mium intermetallics. Typically the calculated spin moment agrees well with experiment, whereas the orbital moment is underestimated by 30–40%. The calculations thus indicate that the spontaneous moment of UCoAl in the experimental field of 7 T is far from saturation, and we can expect a further increase of the moment at higher fields.<sup>11</sup> On the other hand, the XMCD-deduced magnetic moments and those calculated for UPtAl exhibit a somewhat better agreement. We note that no corrections for the orbital polarization were made in the calculations, which would otherwise lead to an increase of the orbital moment. Orbital polarization could be treated using the local density approximation (LDA) +  $U$  scheme.<sup>26</sup> However, such a scheme contains two adjustable parameters, namely, the Hubbard  $U$  and exchange  $J$  terms. In the present work we prefer the simple LSDA potential, which indeed does not describe the orbital polarization quite accurately but is still a first-principles method without any adjustable parameter.

Despite the above discrepancy the overall shapes of the calculated and experimental XMCD spectra correspond well to each other. Since the XMCD spectra of UPtAl and UCoAl show a similarity with only quantitative differences, we discuss them together in what follows. The smaller magnitude and different shape of the  $M_5$  line as compared to the  $M_4$  line results from the almost empty uranium  $5f_{7/2}$  states; see Fig. 6. The main contribution to the  $M_5$  line comes from transitions to spin-split states with  $j_z = \pm 7/2$ . Their contributions to the XMCD have opposite signs and cancel one another to some extent and, as a result, an  $s$ -shaped spectral line with both the negative and positive peaks is observed. The  $M_4$  line comes from the transitions to  $5f_{5/2}$  states, which lie at the Fermi level and are partially occupied. The cancellation between contributions of  $j_z = \pm 5/2$  is suppressed by unbalanced occupations of the corresponding final states due to the spin-polarization, which leads to a single peak shape of the  $M_4$  line.

In conclusion of this section, first-principles calculations are shown to quite reasonably reproduce both  $M_4$  and  $M_5$  edges in the experimental XMCD spectra. The  $M_5$  edge exhibits an asymmetric spectral band with both positive and negative peaks, the shape of which is closely connected to the electron population of  $f_{5/2}$  and  $f_{7/2}$  subbands and to the position of the Fermi level. The calculated density of states displayed in Fig. 6 shows, in agreement with calculations of the paramagnetic ground state,<sup>20,27,28</sup> that the Fermi level is situated close to the bottom of the  $f$  band in both studied compounds, and that states close above the Fermi energy have predominantly  $5f$  character.

#### IV. CONCLUSIONS

In this paper the results of a study of x-ray magnetic circular dichroism of uranium intermetallic compounds UCoAl and UPtAl have been presented. Both systems are of current interest in the field of strongly correlated magnetic and anisotropic systems. The unusual behavior of the UCoAl metamagnetic compound, that exhibits ferromagnetic order only at external magnetic fields and low temperatures, has motivated intensive research in recent years.

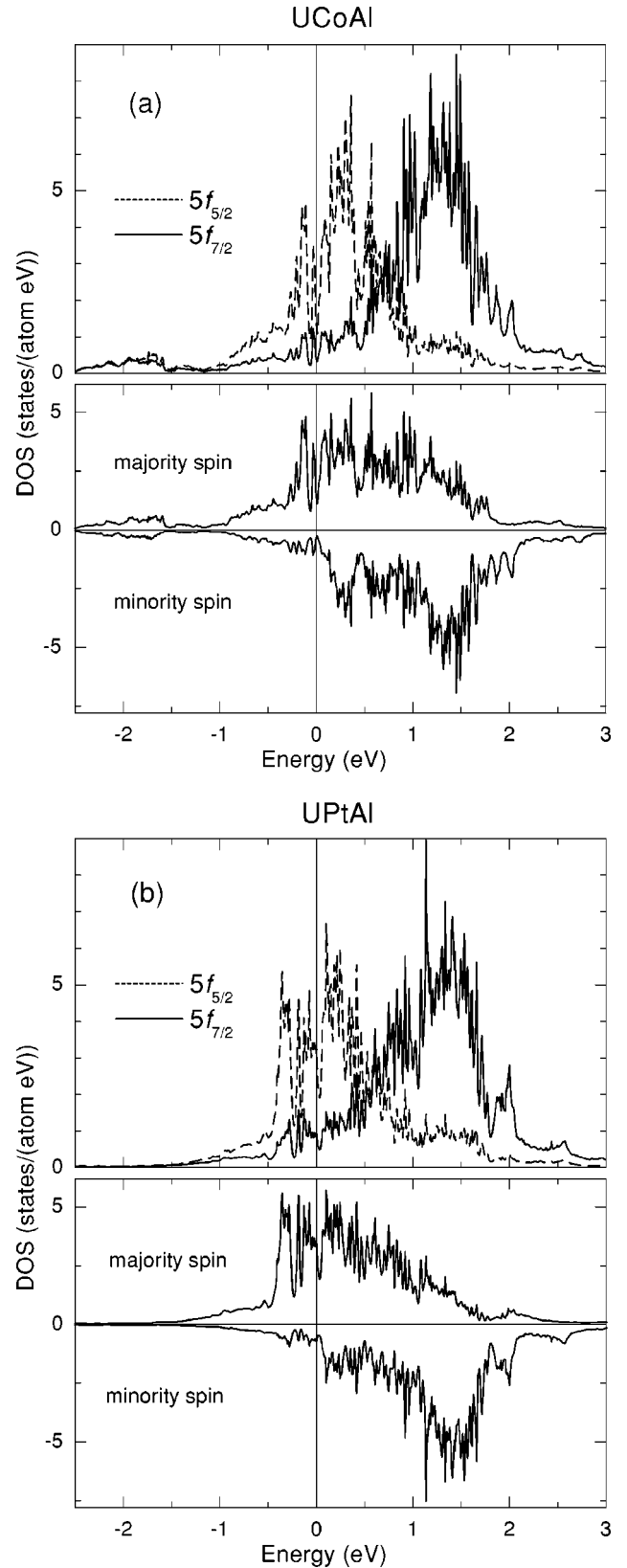


FIG. 6. The partial densities of states of the  $5f_{5/2}$  and  $5f_{7/2}$  states and the total  $5f$  densities for the minority and majority states in UCoAl (a) and UPtAl (b). The Fermi level is at  $E=0$  eV.



Reported quantitative results inferred from the XMCD spectra are based on a sum rule analysis of the spin-orbit split spectra of core levels of uranium. The sum rules enabled us to estimate the spin and orbital components of the uranium ions. These components are antiparallel with the magnetic moment dominated by the orbital part. We notice that a reliable quantity that can be extracted from the sum rule analysis is the ratio between orbital and spin moments and their relative orientation. The values of magnetic moments rather rely on theoretical inputs such as the number of holes in the  $5f$  subshell and a value of the dipolar term. In particular, the spin moment is retrieved, with a higher relative error, as discussed in the text. Comparing the XMCD-derived moments with the results of polarized neutron diffraction and first-principles calculations, we obtained smaller moments from the XMCD sum rules particularly for UCoAl. This indicates that the measured spontaneous magnetic moment of UCoAl is far from saturation, and its further increase should be expected at high fields. The XMCD results proved that the increasing spontaneous moment of UCoAl above the metamagnetic transition arises due to the simultaneous increase of both the orbital and spin uranium  $5f$  moments, leaving the orbital-to-spin magnetic moment ratio  $\mu_L/\mu_S$  roughly unchanged. Furthermore, this ratio appears to be conserved both in ferromagnetic and paramagnetic states al-

though the  $\mu_S$  value in the former case is at least five times larger. On the other hand, the  $\mu_L/\mu_S$  ratio is of comparable values in both studied compounds, close to  $-2$ , though the moments in UCoAl are strongly reduced with respect to those in UPtAl. Similar values of the  $\mu_L/\mu_S$  ratio were also found for other isostructural compounds: UNiGa, UNiAl, and URhAl.<sup>29,30</sup> Our results favor the  $5f^3$  electron configuration in both studied compounds. The reduction of the  $\mu_L/\mu_S$  ratio compared to the  $U^{3+}(5f^3)$  free ion value of  $-2.57$ , and the sizable decrease of orbital and spin moments, especially for UCoAl, indicate a significant delocalization of the  $5f$ -electron states.

The first-principles calculations of the x-ray absorption and XMCD spectra reproduce the experimental data well, including the spectral shapes and structure of both the  $M_4$  and  $M_5$  lines. The shape of the spectral lines at  $M_{4,5}$  edges is closely related to the occupancy of  $f_{5/2}$  and  $f_{7/2}$  subbands and to the position of the Fermi level with respect to the  $5f$  partial states.

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