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5f-hybridization in URhAl studied by X-ray magnetic circular dichroism

W. Grange[a,]*, M. Finazzi[b], J.-P. Kappler[a,c], A. Delobbe[c], G. Krill[c], Ph. Sainctavit[c,d], J.-P. Sanchez[e], A. Rogalev[b], J. Goulon[b]

[a]*Institut de Physique et Chimie des Matériaux de Strasbourg-Groupe d'Etude des Matériaux Métalliques, 23 rue du Loess, 67037 Strasbourg, France*
[b]*European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble Cedex, France*
[c]*Laboratoire pour l'Utilisation du Rayonnement Electromagntique, Bâtiment 209D, Université Paris-Sud, 91405 Orsay Cedex, France*
[d]*Laboratoire de Minéralogie et Cristallographie de Paris, CNRS URA9, Universités de Paris 6 et 7, 75252 Paris, France*
[e]*CEA-Département de Recherche Fondamentale sur la Matière Condensée, SPSMS, 38054 Grenoble Cedex 9, France*

Abstract

We report X-ray magnetic circular dichroism experiments performed at the U–$M_{4,5}$ edges of an URhAl single crystal. Thanks to the sum rules, we derive an orbital magnetic moment on the uranium atoms equal to $(1.63\pm0.14)\mu_B$. The comparison of the shape of the M_5 dichroic signal with pure *J* multiplet calculations shows effects due to 5f-hybridization. However, we found that the contribution of the magnetic dipole term $\langle T_Z \rangle$ to the effective spin moment $\langle S_Z^{\mathrm{eff}} \rangle = \langle S_Z \rangle + 3\langle T_Z \rangle$ is non negligible. These results indicate an higher localization of the 5f-orbitals with respect to other itinerant ferromagnetic actinides compounds such as UFe_2 or UNi_2. © 1998 Published by Elsevier Science S.A.

1. Introduction

In these last years, many experimental and theoretical studies have been devoted to the understanding of the magnetic behavior of actinide (A) compounds. The character of the 5f-states, which is strongly affected by the interatomic A–A distance and the nature of the ligands, gives rise to a wide variety of magnetic behaviors, intermediate to the case of transition and rare earth metals [1]. For example, the ternary compounds crystallizing in the ZrNiAl type like structure with general UTX composition (T is a transition metal and X=Al, Ga, Ge, Sn) present ferromagnetic orderings (UPtAl, URhAl), antiferromagnetic (UNiAl) or paramagnetic behaviors (UFeAl, URuAl) [2,3]. An interesting question which should be addressed is whether the 5f wave functions are localized or if they participate in chemical bonding: Lander [4] showed that valuable information about this behavior can be simply obtained from the ratio of the orbital μ_L to spin μ_S moments: the reduction of $-\mu_L/\mu_S$ (compared to the ratio obtained in a localized approach) occurs principally through the reduction of μ_L, which in turn is the consequence of 5f delocalization.

In this paper, we present X-ray magnetic circular dichroism experiments performed on an URhAl single crystal. The sum rules for XMCD [5,6], that simply relate the integrated magnetic circular dichroism to the orbital and spin magnetic moment in the ground state, together with multiplet calculations demonstrate that the degree of 5f hybridization is substantially reduced, as compared to strong itinerant ferromagnets such as UFe_2 [7–9].

URhAl crystallizes in the ZrNiAl structure and is a ferromagnet with a Curie temperature $T_C=27$ K. An ordered magnetic moment of $\approx 0.94\mu_B$ per unit formula along the easy axis of magnetization (*c* axis) has been reported by Veenhuizen et al. [10]. Angle-dependent macroscopic magnetization measurements give evidence for a huge magnetocrystalline anisotropy, which is the consequence of the large spin orbit coupling: As demonstrated by the cosine variation, the magnetic moment remains aligned with the easy axis of magnetization (Fig. 1). Previous neutron scattering experiments [11] carried out on a single crystal found $\mu_L=2.10\mu_B$ and $\mu_S=-1.16\mu_B$ on uranium atoms yielding a ratio of $-\mu_L/\mu_S=1.81$. This value demonstrates the presence of hybridization effects since in the intermediate coupling scheme $-\mu_L/\mu_S$ is equal to 3.33 ($5f^2$) or 2.54 ($5f^3$). These experiments were in relatively good agreement with recent fully self-consistent band structure calculations including both spin orbit coupling and orbital polarization ($\mu_L=1.61\mu_B$ and $\mu_S=-1.01\mu_B$) [12].

A good description of the magnetic properties is given

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*Corresponding author. E-mail: grange@atlas.u-strasbg.fr

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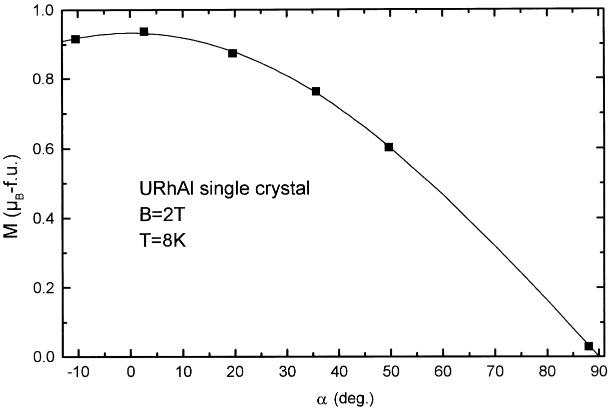

Fig. 1. Total magnetic moment (μ_{total}) measured in an applied magnetic field of $2T$ (squares) as a function of the angle α between the c axis and the applied field. The full curve represents the fitting with a cosine function.

by the variation of the specific heat $C(T)$ presented in Fig. 2. For $T \le 20$ K, $C(T)/T$ is fitted by: $0.076+0.00476T^{3/2}\exp(7/T)$, characteristic of a ferromagnetic magnon spectrum ($T^{3/2}$) with a gap $\Delta=7$ K due to magnetic anisotropy [13].

2. Experiments

The XMCD signal was measured by monitoring the total fluorescence yield (FY) signal over the U–$M_{4,5}$ edges ($3d^{10}\ 5f^{n} \rightarrow 3d^{9}\ 5f^{n+1}$). The experiments were carried out at the ESRF on the ID12A beamline, which is dedicated to polarization dependent XAFS studies [14]. The source was the helical undulator Helios-II which provides high flux, high circular polarization rate (about 0.9) and tunable helicity of the incoming beam. After reflection on two Si(111) crystals, the rate of circular polarization falls to about 0.35 at the M_5 edge and 0.45 at the M_4 edge. The sample was cooled down to 8 K, the direction of the applied magnetic field ($2T$) was parallel to the direction of the incoming beam and the X-ray incidence angle was 13° with respect to the c axis.

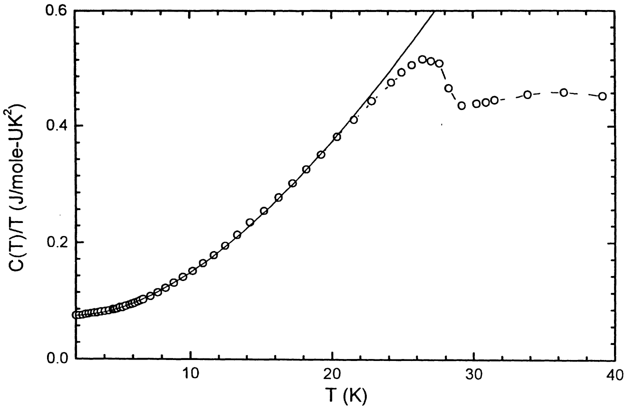

Fig. 2. Temperature dependence of the specific heat (open circles), characteristic of a ferromagnetic magnon spectrum ($T^{1/2}$) (full curve).

For an accurate analysis, the X-ray absorption coefficient was measured in partial electron yield detection mode on beamline D41 at the French synchrotron radiation facility (LURE).

3. Results and discussion

Fluorescence yield detection (FY) is known to be a suitable detection mode in the presence of a strong magnetic field or for dilute samples [15]. However, in the case of bulk samples, FY suffers from the so-called 'self-absorption effects', leading to an attenuation of the white line in the absorption coefficient. Several data corrections have to be done in order to extract the absorption coefficient [16] which can be performed in a straightforward manner by comparison with the isotropic spectrum $\mu(E)$ measured in electron yield detection.

In Fig. 3, we present the isotropic absorption coefficient and the XMCD signal corrected for the finite rate of circular polarization. First, a comparison of the shape of the XMCD signal with pure J multiplet calculations in O_3 symmetry (shown in Fig. 4) is an interesting tool to study the degree of hybridization: In actinides, the crystal field

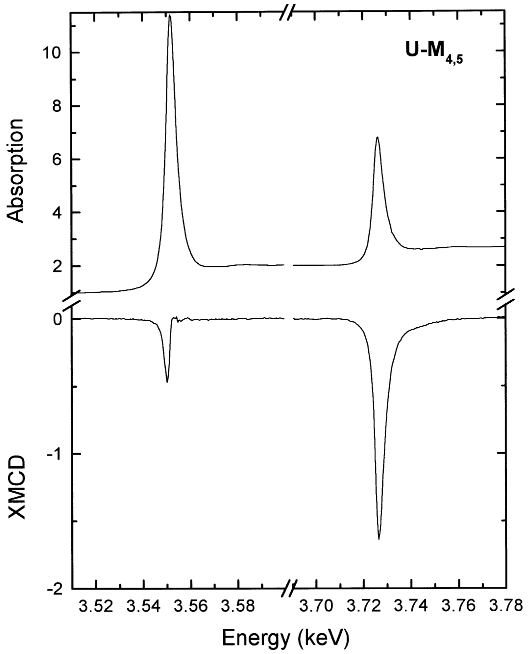

Fig. 3. U–$M_{4,5}$ isotropic absorption spectra and dichroism of URhAl. The dichroism signal was measured using total fluorescence yield detection and corrected for self absorption effects and energy dependence of the circular polarization. The isotropic spectrum, measured in total electron yield detection on the same sample, was scaled so that the jump far above the M_5 edge is 1. For the XMCD experiments, the c axis of the sample was titled at 13° away from the incident X-ray beam direction.

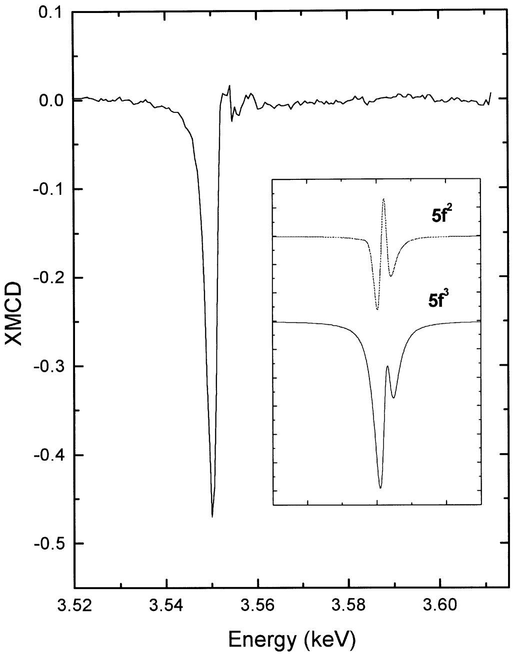

Fig. 4. Experimental U–M_5 dichroism and comparison with calculated shape for $5f^2$ and $5f^3$ configurations. The calculations are performed using Cowan's code taking into account the life time broadening (convolution with a Lorentzian function, FWHM=2 eV) and the experimental resolution (0.3 eV).

interaction is generally much smaller than the fine structure spitting; therefore, we emphasize that the introduction of this interaction in the full Hamiltonian may reduce μ_L and μ_S but keep the $-\mu_L/\mu_S$ ratio constant. As a result, the shape of the XMCD signal will not be affected by the symmetry of the full Hamiltonian [17]. Therefore, the fact that these atomic calculations fail to reproduce the XMCD signal demonstrates a certain amount of hybridization.

By applying the first sum rule, which gives the expectation value of the orbital momentum in the ground state, we obtain $\langle L_Z \rangle / n_h$=-(0.14±0.01)$\hbar$, where n_h is the number of holes on the f shell. From band structure calculations, Gatche et al. [12] derived a 5f electron occupation equal to 2.73 yielding to $\mu_L = (1.63 \pm 0.14)\mu_B$.

The second sum rule allows the determination of the spin momentum as long as the magnetic dipole term $\langle T_Z \rangle$, which is related to the anisotropy of the spin charge distribution around the nucleus, is known. In the case of itinerant systems and for cubic symmetry, it has been shown by band structure calculations and many experiments [18,19] that the contribution of $\langle T_Z \rangle$ to the effective spin momentum $\langle S_Z^{\mathrm{eff}} \rangle = \langle S_Z \rangle + \lambda \langle T_Z \rangle$ (with $\lambda = 3$ for the U–$M_{4,5}$ edges) is negligible. We made this naive assumption and got $\mu_S = -(1.90 \pm 0.14)\mu_B$ which would yield to a total magnetic moment $\mu_S + \mu_L$ antiparallel to the magnetic field in total disagreement with both neutron diffraction data and band structure calculations.

Recently, Van der Laan and Thole have computed the value of $\langle T_Z \rangle$ in the intermediate coupling scheme and found $\langle T_Z \rangle = 1.16 \langle S_Z \rangle$ for a $5f^2$ configuration and $\langle T_Z \rangle = 0.62 \langle S_Z \rangle$ for a $5f^3$ configuration [20]. Since the results of the multiplet calculations indicate an admixture of $5f^2$ and $5f^3$ configurations, $\langle T_Z \rangle$ remains an unknown quantity and μ_S has to be evaluated in another way: Band structure calculations and neutron experiments [21,11] have shown that the Rh-4d magnetic moment, which is entirely due to the strong 5f–4d hybridization, is expected to be small ($\mu_{Rh} \approx 0.1\mu_B$). Assuming an almost total cancellation of the Rh and conduction electrons magnetic moments (an analysis of electronic structure and hybridization shows that the transition metals and uranium spin moments have to be antiparallel [22]), we derive from the macroscopic magnetic moment ($\mu_{\mathrm{total}} = 0.94\mu_B$) a spin moment on the U atoms equal to $(0.69 \pm 0.14)\mu_B$. These findings are in poor agreement with previous neutron diffraction experiments, which seem to overestimate both the spin and orbital magnetic moments, as already reported by theoretical investigations.

From the value of the uranium spin and orbital moment, we obtained $-\mu_L/\mu_s = 2.36$ and $\langle T_Z \rangle = 0.57 \langle S_Z \rangle$. These result tend to suggest a small 5f hybridization, but the large uncertainties (as high as ±30%) cannot allow us to determine with accuracy the degree of the 'chemical bonding'. However, the calculations of the M_5 dichroism together with the failure of the assumption of a negligible value of $\langle T_Z \rangle$ indicate obviously that the 5f-wave functions delocalization is intermediate between the case found in $USb_{0.5}Te_{0.5}$ [23] (localized magnetism) and UFe_2 (itinerant magnetism).

For the UTX compounds, where the bonding between U and T atoms determine the magnetic properties, new information concerning 5f–4d hybridization could be provided by a knowledge of the precise value of the Rh spin and orbital moments. In this respect, we are attempting to perform XMCD experiments at the Rh–$L_{2,3}$ edges.

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