Direct Evidence of the Role of Hybridization in the X-Ray Magnetic Circular Dichroism of α-Ce

M. Finazzi,[1] F. M. F. de Groot,[2] A.-M. Dias,[1] B. Kierren,[3] F. Bertran,[3] Ph. Sainctavit,[1,4] J.-P. Kappler,[1,5] O. Schulte,[6] W. Felsch,[6] and G. Krill[1]

[1]*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université Paris-Sud, 91405 Orsay Cedex, France*

[2]*Solid State Physics, University of Gröningen, Nijenborgh 4, 9747 AG, Gröningen, Netherlands*

[3]*Laboratoire de Physique du Solide, CNRS URA DO 155, Université de Nancy 1, 54506 Vandoeuvre les Nancy Cedex, France*

[4]*Laboratoire de Minéralogie et Cristallographie de Paris, CNRS URA9, Universités de Paris 6 et 7, 75252 Paris Cedex 05, France*

[5]*Institut de Physique et Chimie des Matériaux de Strasbourg-Groupe d'Etude des Matériaux Métalliques, 23 rue du Loess, 67037 Strasbourg, France*

[6]*I. Physikalisches Institut, Universität Göttingen, Bunsenstrasse 9. 37073 Göttingen, Germany*

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We present an x-ray magnetic circular dichroism (XMCD) study of a [Ce(10 Å)/Fe(30 Å)] multilayer performed at the Ce-$M_{4,5}$ absorption edges. In this system the Ce-4f electrons are strongly hybridized with the valence band. XMCD experiments show that they carry an ordered magnetic moment. The differences of the shape of the XMCD signals of a typical γ-like compound (CeCuSi) and of the Ce/Fe multilayer highlight the role of hybridization in determining the ground state of cerium atoms in the multilayer, which results in a mixing of $J = \frac{5}{2}$ and $J = \frac{7}{2}$ coupled states.

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Magnetic circular dichroism in x-ray absorption (XMCD) is now widely used to investigate the local magnetic properties of molecules or of solids both in the bulk or at the surface. This technique combines the orbital and site selectivity of a conventional absorption experiment with the possibility of reversing the relative orientation of the sample magnetization and the helicity of the photons. Due to the electric dipole selection rules, which govern the absorption process of polarized light, orbital- and element-projected magnetic moments can be deduced in both magnitude and direction [1].

In this Letter, we want to focus on a fundamental problem related to the magnetic properties of cerium atoms in highly correlated systems. Our goal is to give clear evidence that *XMCD experiments performed at the $M_{4,5}$ absorption edges of cerium are able to highlight the role of hybridization in the 4f magnetic properties of such systems.* The archetype for a highly correlated system is the case of cerium metal itself, in the so called α state [2]. In α-Ce, the 4f electron states of cerium are strongly hybridized with the 5d conduction electrons, and this hydridization usually yields a nonmagnetic ground state even at low temperature. Several experiments [3–5] and calculations [6,7] lead to the conclusion that the ground state of α-like Ce can be magnetically ordered in 3d intermetallic compounds such as $CeFe_2$ and $CeCo_5$. Indeed, by XMCD experiments at the Ce $M_{4,5}$ edges, we demonstrated unambiguously that a small 4f magnetic moment (about $-0.15\mu_B$) develops on cerium in $CeFe_2$ [4].

X-ray absorption (XAS) experiments performed on Ce-Fe multilayer systems [8] at the Ce-$L_{2,3}$ absorption edges have revealed that in these multilayers *the cerium is in the α phase in a region extending up to 25 Å from the interface* [9]. It has been suggested that Ce near the interface adopts the α-phase electronic configuration and hence a smaller atomic volume to reduce the misfit and strain at the interface. XMCD experiments performed at the Ce-$L_{2,3}$ edges clearly demonstrate the existence of a magnetic moment of 5d origin on the cerium atoms on a depth scale of at least 15 Å near the interface and coupled antiparallel to the moment of iron [9].

We must emphasize that the spectral shape of any rare-earth isotropic $M_{4,5}$ absorption edge is a fingerprint of the initial value of the total angular momentum quantum number J in the ground state (for the pure $4f^1$ state of Ce, $J = \frac{5}{2}$). As a consequence of the Wigner-Eckart theorem, *the isotropic spectral shape will not change as long as the ground state remains characterized by a single J value* [10]. Thus any modification in the isotropic line shape is direct evidence that levels with different values of J contribute to the ground state. As shown in our recent paper [10], this remains true also for XMCD spectra. The aim of this Letter is to demonstrate that the *ground state* of α-Ce is described by a combination of the $4f^0L$, $4f^1_{J=5/2}$, and $4f^1_{J=7/2}$ configurations (where L represent an electron in the conduction band) as a result of the hybridization of the f electrons with the conduction band. This has already been suggested by previous theoretical works [11,12], but a direct experimental proof was still lacking.

For γ-like Ce compounds the crystal field parameter is much smaller than the energy separation between the two spin-orbit split $J = \frac{5}{2}$ and $J = \frac{7}{2}$ states (typically 10 meV against 250 meV, respectively [13]). In the case of α-like cerium, previous $M_{4,5}$ XAS experiments [14] have proven that the hybridization and the spin orbit can be of the same order of magnitude. The delocalization of the 4f electrons leads to the double result of reducing the effective separation between the $J = \frac{5}{2}$ and the $J = \frac{7}{2}$ levels and

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increasing the influence of the crystalline environment. A recent XMCD study shows the importance of the interplay between hybridization and crystal field in determining the magnetic properties of $CeRh_3B_2$ [15]. Thus a correct description of the nature of the ground state of α-Ce needs to properly take into account both hybridization and crystal field effects with a basis set which should include the $4f^0L$, $4f^1_{J=5/2}$, and $4f^1_{J=7/2}$ configurations. We shall refer to some general results through an advanced theoretical model.

The Ce-$M_{4,5}$ XMCD data were obtained on the SU22 beam line of the Super-ACO storage ring at LURE (Orsay, France). The Ce XAS spectra were recorded in the *transmission mode* on a Ce-Fe multilayer consisting of twelve [Ce(10 Å)/Fe(30 Å)] periods evaporated on a 7-μm-thick Be foil after deposition of a 50 Å chromium buffer, and was covered by a 200 Å thick chromium layer. The experiments are performed at 77 K under $\mathbf{B} = \pm 50$ mT magnetic field, which is high enough to saturate the total magnetic moment in the plane of the multilayer [16]. The angle between the sample normal and the light propagation vector was 30°. The rate of circular polarization is estimated to be $(25 \pm 1)\%$ and $(17 \pm 1)\%$ at the M_5 and M_4 edges, respectively [17]. The XMCD spectra are obtained by the difference between the absorption data recorded for two opposite directions of the magnetic field, which is reversed for each photon energy.

In Fig. 1 we present the Ce-$M_{4,5}$ isotropic (upper panel) and XMCD (lower panel) spectra obtained for the multilayer. As a reference, we also show the corresponding spectra of a typical γ-like Ce system. Since metal γ-Ce is not magnetic, we have chosen the spectra obtained on polycrystalline CeCuSi in the total electron yield mode [4]. As evident in Fig. 1(a), the isotropic signal from the multilayer is characterized by a strong hybridization satellite emission (the so-called $4f^0$ channel) at $h\nu = 890$ and 908 eV, which confirms that Ce in the multilayer is in the α phase. The analysis of the dichroic signal demonstrates that the $4f$ electrons carry a magnetic moment. When compared to CeCuSi, the isotropic spectrum of the Ce/Fe multilayer shows a larger energy separation between the M_4 and M_5 maxima. A second feature is the smearing out of the atomic multiplet fine structures at correspondence both with the M_4 and the M_5 edges. At the M_4 the small peaks on the low photon energy side of the white line are not resolved anymore, while at the M_5 the doublet collapses into a single peak. The multilayer and the CeCuSi compound also present a different branching ratio between the isotropic intensities of the M_4 and M_5 absorption edges. This result is well confirmed by transmission experiments on a 150 Å metal γ-Ce film in experimental conditions strictly comparable to the ones for the Ce/Fe multilayer.

Although the multiplet structures of the isotropic M_4 absorption-edge signal of the multilayer are smeared out, the corresponding XMCD signal presents a similar

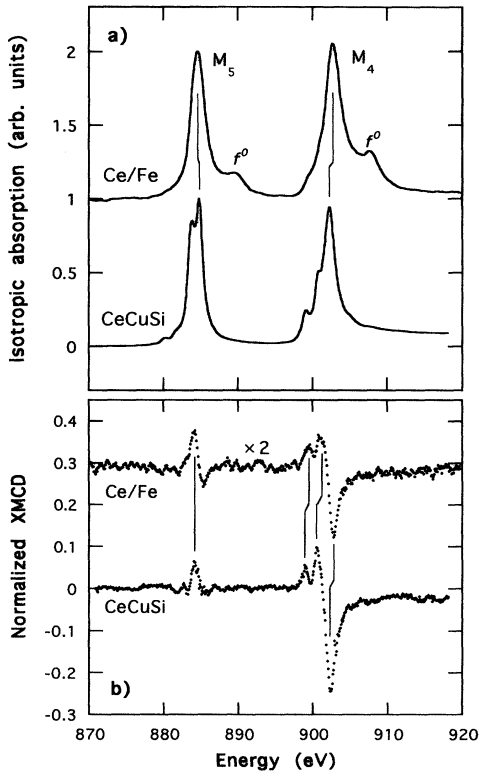

FIG. 1. Isotropic (upper panel) and XMCD (lower panel) spectra obtained for a Ce(10 Å)/Fe(30 Å) multilayer and CeCuSi [4] at the Ce-$M_{4,5}$ absorption edges. The intensity of the M_5 edge isotropic spectra of the two samples has been arbitrarily set to unity. The XMCD spectra have been normalized to 100% circular polarization rate.

line shape as the γ-like compound, and the atomic fine structure is still well resolved. A closer investigation reveals that the XMCD signal at the M_4 edge of the multilayer is shifted towards high photon energies by 0.15 eV. At the M_5 edge we observe the presence of a negative peak absent in the dichroic spectrum of CeCuSi. This feature has not been observed before in other γ- or α-Ce systems and is not reproduced by one-configuration atomic models at $T = 0$ [18]. Since the spectral shape of the XMCD signal cannot be changed as long as the ground state remains in a pure $J = \frac{5}{2}$ value, and since the $4f^0L$ configuration is not observed to contribute to the dichroic signal [4], *we have direct evidence of the presence of the* $J = \frac{7}{2}$ *term in the ground state of the cerium atoms in the multilayer.*

In Fig 2 we show the isotropic and XMCD spectra of the $J = \frac{5}{2}$ and $J = \frac{7}{2}$ configurations of Ce^{3+}, using an atomic multiplet calculation of the $4f^1_{J=5/2} \rightarrow 3d^94f^2$ and $4f^1_{J=7/2} \rightarrow 3d^94f^2$ transitions [18]. The sign of the exchange field acting on the spin of the $4f$ electrons is chosen in order to reproduce the antiparallel alignment of

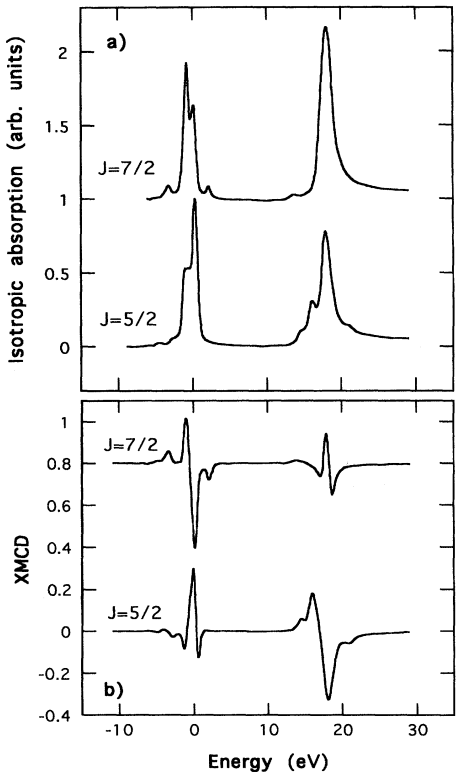

FIG. 2. Ce-$M_{4,5}$ isotropic (top panel) and XMCD (lower panel) spectra obtained for the $J = \frac{5}{2}$ and $J = \frac{7}{2}$ states calculated for the ion Ce^{3+}. The zero of the energy axis has been chosen at correspondence with the maximum in the M_5 edge of the $J = \frac{5}{2}$ XMCD spectrum. The intensity of the M_5 edge of the $J = \frac{5}{2}$ isotropic spectrum has been set to unity.

the Fe-3d and Ce-4f spin moments expected for Ce-Fe systems [5,6,9]. Unfortunately, the experimental XMCD and isotropic spectra cannot be described in terms of a simple combination of $J = \frac{7}{2}$ or $J = \frac{5}{2}$ because of the presence of interference terms, but a qualitative analysis is still possible [11]. The dichroic signal of CeCuSi is well described by the XMCD spectrum given by the $J = \frac{5}{2}$ state [4]. On the contrary, the experimental isotropic M_5 edge is not an exact replica of the calculated $J = \frac{5}{2}$ spectrum. This is due to a small hybridization of the f electrons with the valence band [11]. These effects are not taken into account by the ionic model we used, and seem not to influence significantly the XMCD signal of γ-like Ce. For the multilayer, the appearance of a negative peak in the XMCD signal can be interpreted in terms of a contribution from the $J = \frac{7}{2}$ configuration. Note also that the possible presence of the $J = \frac{7}{2}$ contribution would lead to a decreasing of the M_5/M_4 branching ratio in the isotropic spectrum, as actually observed in our experimental data.

In order to study the influence of hybridization on the XAS and XMCD of α-Ce, we used the charge transfer multiplet (CTM) model as developed for Ce compounds by Jo and Kotani [19]. This model mixes $4f^1$ with $4f^0L$ for the ground state and $3d^94f^2$ with $3d^94f^1L$ for the final state. The ground and final state mixing is controlled by the energy separations and the hybridization. For the calculation reported in Fig. 3 we used a $4f^1$ state at 1.7 eV below the $4f^0L$ band, which was approximated by a single level. In the final state the center of gravity of the $3d^94f^2$ multiplet is 4.7 eV below the $3d^94f^1L$ multiplet. The spherical hybridization used was 0.38 eV. These numbers are the same as the ones in the CTM calculation of $CeRh_3$ in Ref. [19]. To include nonspherical symmetry a small octahedral crystal field was added, and an exchange field of 5 meV was used to create the XMCD spectra. The used crystal and exchange field values have no physical significance and are taken just to show the effects of symmetry reduction. With this choice of parameters, we obtain a ratio between the weights of the $J = \frac{7}{2}$ and $J = \frac{5}{2}$ terms

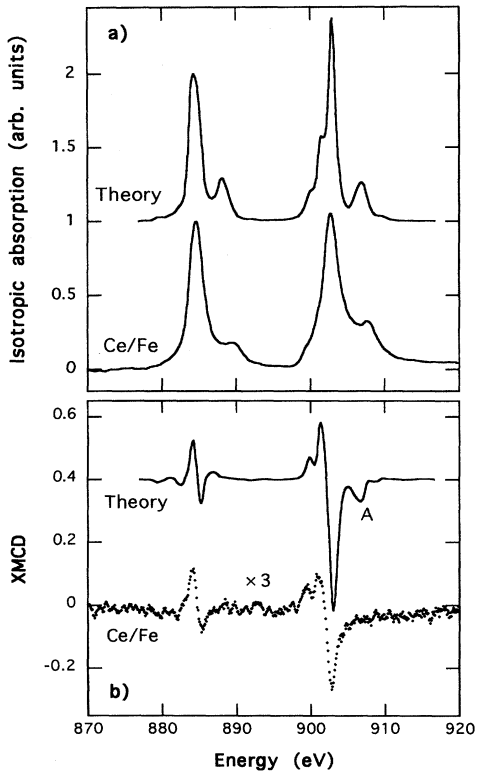

FIG. 3. Comparison between the experimental data of the Ce/Fe multilayer and the results of the model described in the text. Top panel, Ce-$M_{4,5}$ isotropic spectra; lower panel, XMCD spectra. The intensity of the two M_5 edge isotropic spectra has been set to unity. The origin of the energy axis of the theoretical spectra has been chosen in order to align the positive peaks at correspondence with the M_5 edge of the theoretical and experimental XMCD spectra.

in the ground state equal to 0.10–0.15 [12]. In Fig. 3, the experimental data obtained on the Ce/Fe multilayer are compared to the isotropic and XMCD spectra, calculated according to this model. The experimental isotropic and XMCD line shapes are qualitatively well described at both the M_4 and M_5 edges, even if the intensity of the M_4 is overestimated. For the isotropic spectra, the theoretical model reproduces the variation of the M_4-M_5 energy separation and the position of the f^0 satellite. In the XMCD spectrum of α-Ce, the negative peak at the M_5 edge is reproduced correctly, as well as the shift of the M_4 XMCD multiplet towards the higher photon energies. However, the intensity of the experimental dichroic signal is about a factor of 3 weaker than the experimental one. This may be due to a decreasing of the $4f$ moment across the cerium layer. Nevertheless, we find a similar ratio between the experimental and theoretical XMCD intensities of CeCuSi. For γ-like Ce, this behavior reflects the reduction of the $4f$ magnetic moment due to the crystal field-induced mixing of the Zeeman levels in the ground states. This phenomenon is probably underestimated by the model used in Fig. 3. The presence of the peak labeled by the letter A in Fig. 3(b) indicates that the XMCD effect is partly transferred to the satellite structure. If the valence states of the system had been described with a continuous band instead of a single discrete level, feature A would have been broadened into a shoulder.

The discussion of the results of the application of the sum rules of Ref. [1] to the XMCD signal will be given elsewhere. We would like to anticipate that $\langle S_z^{4f} \rangle$ is found to be aligned antiparallel to $\langle L_z^{4f} \rangle$ and to $\langle S_z^{3d} \rangle$.

In conclusion, we have presented a XMCD study of a [Ce(10 Å)/Fe(30 Å)] multilayer performed at the Ce-$M_{4,5}$ absorption edges. In this system, the Ce atoms are in the highly hybridized α-phase, characterized by a strong mixing between the $4f$ electrons with the valence band, and carry an ordered magnetic moment. XMCD experiments show the part of this moment is due to $4f$ electrons. The differences in the shape of the XMCD signals of a typical γ-like compound (CeCuSi) and of the Ce/Fe multilayer demonstrate that the XMCD spectra reflect the hybridization in the ground state of the cerium atoms in the multilayer, which results in a mixing of $J = \frac{5}{2}$ and $J = \frac{7}{2}$ configurations. The experimental isotropic and XMCD spectra are well described in terms of a model which combines the Anderson impurity Hamiltonian with the interactions described by the Slater integrals, spin orbit coupling, and crystal field.

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