

Influence of hybridization in the Magnetic Circular X-ray Dichroism at the Ce-M_{4,5} absorption edges of Ce-Fe systems

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We have performed a Magnetic Circular X-ray Dichroism (XMCD) study at the Ce-M_{4,5} absorption edges on some Ce-Fe systems. We find that the dichroism signal in these systems is very sensitive to the degree of hybridization of the 4*f* electrons with the valence band. XMCD is able to demonstrate that the ground state of Ce in the more strongly hybridized systems results in a mixing of atomic $J=5/2$ and $J=7/2$ states.

1. INTRODUCTION

In recent years the study of the electronic and magnetic properties of Ce and of Ce intermetallic compounds with high energy spectroscopies has received increasing attention. The reason is that, although *f* electrons are usually treated as localized (as, for example, for metallic Ce in the so-called γ -phase), there are some cases in which the Ce *f*-states are strongly coupled to the conduction band giving rise to unusual properties [1]. In these systems, the strong hybridization of the Ce 4*f* electron states with the 5*d* conduction electrons usually yields a non magnetic ground state even at low temperature. In the past, several experiments [2,3,4] and calculations [5] lead to the conclusion that the ground state of α -Ce can be magnetically ordered in 3*d*-intermetallic compounds, like CeFe₂. For these reasons, the investigation of the contribution of the 4*f* electrons to the

magnetic moment is a very crucial topic in the field of magnetism of cerium compounds and of correlated systems in general. Such a study is made possible by means of Magnetic Circular Dichroism in X-ray absorption (XMCD). XMCD is a spectroscopic technique which combines the site and orbital selectivity, typical of absorption spectroscopy, to a direct insight of the magnetic fine structure of the absorption edges. All these reasons, together with the existence of sum rules that allow to calculate the ground state, orbital projected $\langle L_z \rangle$ and $\langle S_z \rangle$ expectation values [6], make XMCD a powerful instrument to study the magnetic properties of solid state materials.

Here 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 a clear evidence that XMCD experiments performed at the M_{4,5} absorption edges of cerium are able to highlight the role of hybridization on the 4*f*

magnetic properties of such systems. In fact 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 J in the ground state (for γ -Ce: $J=5/2$). As a consequence of the Wigner-Eckart theorem, the spectral shape will not change as long as the ground state remains characterized by a single J value [7]. Thus any modification in this spectral shape is a direct evidence that states characterized by different J values contribute to the ground state. In a recent paper [3], we demonstrate that this remains true for XMCD. In this case, variations of the temperature and of the intensity of the external magnetic field or of the crystal field can only affect the total amplitude of the XMCD spectrum, but not its shape. Thus the influence of hybridization might be correlated to the change in the XMCD spectra. The aim of this paper is to present the evolution of the isotropic and XMCD spectra as a function of the degree of delocalization of the f -electrons in different Ce-Fe systems.

2. EXPERIMENTAL

The Ce-Fe systems we have investigated are: a Ce(10Å)/Fe(30Å) multilayer, Ce_xFe_{1-x} (with $x=0.19$ or $x=0.27$) amorphous alloys, and a bulk $CeFe_2$ polycrystalline sample. Since we ignore the existence of a Ce-Fe compound in which the cerium atoms are in the γ -phase, we choose the spectra obtained on polycrystalline CeCuSi in the total electron yield mode [3] as a reference of a typical γ -Ce system. In this way we can follow the evolution of the isotropic and XMCD spectra as a function of the degree of the hybridization of the f -electrons with the valence band. The multilayer and the alloys were deposited *ex situ* on a mylar or on a parilene substrate respectively and they were protected with a 100 Å thick chromium layer. Their absorption spectra were collected in the transmission mode. The $CeFe_2$ and CeCuSi samples were scraped *in situ* and the data were collected in the total electron yield mode.

The Ce- $M_{4,5}$ XMCD experiments were performed on the SU22 beam line on the asymmetric wiggler of the Super-ACO storage ring at LURE (Orsay, France) [8]. The typical circular polarization rate of the light was ~25% at $h\nu=880$ eV (Ce- M_5) and ~13% at $h\nu=900$ eV (Ce- M_4) 0.3 mrad out of the axis of the insertion device [9]. The XMCD spectra are obtained by the difference between the absorption data recorded for two opposite directions of the magnetic field.

3. RESULTS AND DISCUSSION

In figure 1 we present the isotropic spectra of the different Ce-Fe systems we have investigated. The spectra have been classified from the top to the bottom according to the intensity of the f^0 satellite, which can be taken as an index of the delocalization of the f -electrons. The intensity of the spectra has been arbitrarily normalized at the M_5 maximum.

As the satellite intensity increases, the M_4 edge shifts towards the higher photon energies and the atomic multiplets typical of γ -cerium are smeared out: at the M_4 the small peaks on the low photon energy side of the white line are not resolved any more, while at the M_5 the doublet collapses into a single peak. Both these behaviors have been explained in terms of the increasing hybridization strength, which compress the $4f$ manifold [10]. A second feature is the progressive inversion of the M_4/M_5 branching ratio.

Figure 2 shows the XMCD spectra. A discussion of the absolute intensity of the XMCD signals is not the aim of the present publication and will be treated in a forthcoming paper. Since we will focus essentially on the dependence of the lineshape of the XMCD spectra *vs.* the degree of delocalization of the $4f$ -electrons, the intensity of the spectra in fig. 2 has been normalized to the maximum at the M_5 absorption edge.

The XMCD structures at M_4 are shifted towards the high photon energies as already observed for the isotropic spectra. Note that,

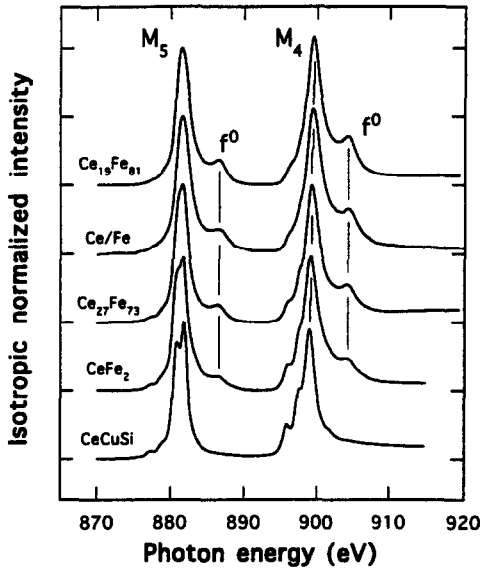


Figure 1. Normalized isotropic Ce- $M_{4,5}$ absorption edges

although the multiplet structures of the isotropic M_4 absorption-edge signal of the multilayer are smeared out, in the corresponding XMCD signal the atomic fine structure is still well resolved. At the M_4 the relative intensity of the peaks show a strong dependence on the particular compound. In the two top spectra of fig. 2, a new feature appears as a negative peak at the M_5 . Since the spectral shape of the XMCD signal cannot be changed as long as the ground state remains in a single $J=5/2$ value, we have a direct experimental evidence of the presence of terms characterized by different J values in the ground state of the cerium atoms of the different systems here reported. Moreover, in some strongly hybridized cerium compounds, previous $M_{4,5}$ XAS experiments [11] have proven that the hybridization and the spin orbit interaction can be of the same order of magnitude. For these reasons, we think that the XMCD of the Ce-Fe systems here reported should be interpreted in terms of a presence of the $4f^0L$, $4f^1(J=5/2)$ and $4f^1(J=7/2)$ configurations (where L represents an electron in the conduction band). This fact

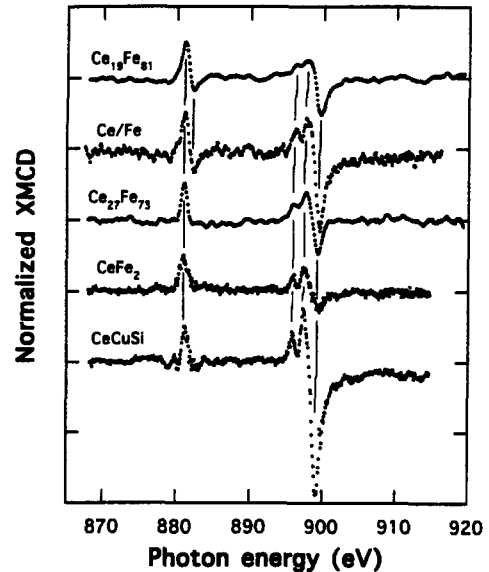


Figure 2. Normalized XMCD at the Ce- $M_{4,5}$ absorption edges

has already been suggested by previous theoretical works [12,13], but a direct experimental proof was still lacking.

In figure 3 we show the isotropic and XMCD spectra of the $J=5/2$ and $J=7/2$ 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 [14]. The sign of the exchange field acting on the spin of the $4f$ -electrons is chosen in order to reproduce the antiparallel alignment of the Fe- $3d$ and Ce- $4f$ spin moments expected for $CeFe_2$ [4,5]. The dichroic signal of CeCuSi is very well described by the XMCD spectrum given by the pure $J=5/2$ state [3]. On the contrary, the presence of a negative peak in the XMCD signal at the M_5 can be interpreted in terms of a contribution from the $J=7/2$ term. Being the magnitude of the dichroic spectrum of the $J=7/2$ level smaller at the M_4 than at the M_5 edge, this term should affect mostly the M_5 edge, without introducing new features at the M_4 . Note also that the possible presence of the $J=7/2$ contribution would lead to a decreasing of the M_5/M_4 branching ratio in the isotropic spectrum, as actually observed

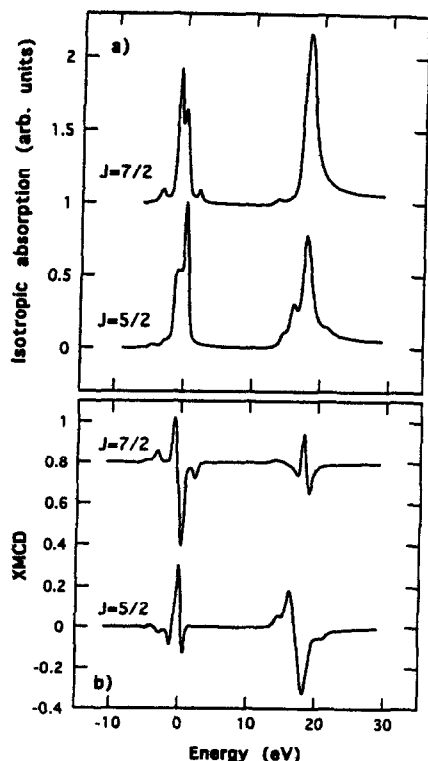


Figure 3. Theoretical isotropic (a) and XMCD (b) spectra of $Ce_{J=5/2}$ and $Ce_{J=7/2}$

in our experimental data. This simple picture, however, fails in justifying the behavior of the dichroism signal at the M_4 edge, where the relative intensity of the multiplets does not show a definite trend. Actually, the dichroism and isotropic signals do not correspond to a simple sum of the contributions due to atomic states with different J , but there are also interference terms [12]. Thus, the complex behavior of the XMCD at the M_4 edge may be the result of the interplay of the $4f^0L$, $4f^1(J=5/2)$ and $4f^1(J=7/2)$ configurations. Therefore, in order to correctly reproduce the shape of the XMCD of these systems, a more sophisticated model is needed, taking explicitly into account the coupling of the f -electrons with the valence band and the electron-electron interactions, which are responsible for the appearance of a multiplet fine structure in the spectra.

4. CONCLUSIONS

In conclusion, XMCD performed at the $Ce-M_{4,5}$ absorption edges on some $Ce-Fe$ systems is very sensitive to the degree of hybridization of the $4f$ electrons with the valence band. It is also able to demonstrate that the ground state of Ce in the systems more strongly hybridized results in a mixing of atomic states characterized by $J=5/2$ and $J=7/2$.

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