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Surface and interface cerium electronic configuration in Ce/Fe (100)

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Abstract. – The cerium electronic configuration of very thin films deposited on Fe(100) has been studied by core level photoemission. In the low-coverage regime (≤ 1 monolayer), cerium atoms are in a trivalent state ($4f^1$ configuration). For larger coverages, cerium atoms exhibit a mixed valent state. This behaviour reflects the valence change of covered cerium atoms at the interface and results from the increase in the hybridization strength for these interface atoms. Owing to an original method, we were able to directly decompose our experimental spectra in two contributions corresponding to the covered ("bulk") and non-covered (surface) atoms.

The spectroscopic properties of cerium systems have been recently a matter of debates and controversies in the literature [1]-[5]. Several fundamental questions are addressed in these studies. The main one is the character of the f states (itinerant or localized) and their appropriate descriptions in terms of two alternative approaches: density functional band approach and model Hamiltonians for strongly correlated electrons like the Anderson model. The electron spectroscopic techniques (photoemission and inverse photoemission) are particularly useful in this puzzle, because they give direct information on the electronic structure and can be compared with theoretical predictions.

However, the electron spectroscopies are surface-sensitive techniques due to the low value of the inelastic mean free path of electrons in solids. Recent investigations on polycrystalline compounds have suggested that the surfaces of highly hybridized systems are in fact nearly trivalent [6]-[8]. These studies are based on the energy dependence of the mean free path λ. Varying degrees of surface sensitivity can then be obtained by changing the photon energy and then the escape depth of the photoelectron. Therefore the surface signal can obscure the results. Most experiments were carried out on polycrystalline materials, whose surface were cleaned by scraping. As a consequence, the surface is poorly characterized, and little is known on its stoichiometry, its disorder and the extension of the perturbed region.

To determine the spectroscopic properties of the bulk, it is very important to study well-characterized systems in order to subtract the surface contribution. Therefore, it is necessary to reconsider this problematic with the help of modern surface techniques. A recent study

on Ce/Pt(111) has shown that an epitaxial compound can be obtained by annealing [9]. On this sample, no surface effect has been observed leading the authors to the conclusion that the crystal surface consists purely of Pt. On the other hand, Ce deposited on W(110) can present a strongly intermediate valence [10] suggesting that the stabilization of the trivalent state at a surface is not a general rule.

In this paper, we present a spectroscopic study of ultra-thin films of Ce (≤ 2 monolayers) deposited on Fe(100). The layer-by-layer growth mode and the absence of diffusion at room temperature make this system highly suitable for the careful study of the Ce electronic configuration as a function of thickness. We show that Ce atoms are nearly trivalent for very low coverage (≤ 1 monolayer) whereas the mean valence increases ($4f$ occupation number n_f decreases) with increasing coverage. By covering cerium with another rare-earth element which has nearly the same non-f electronic configuration, we unambiguously obtain the contribution of the interface to the experimental spectra. This procedure eliminates the surface contribution and allows us to directly determine the electronic configuration of cerium at the interface without any assumption on the electron mean free path.

Cerium has been evaporated onto monocrystalline iron substrates at room temperature and details concerning the sample preparation and growth characterization can be found elsewhere [11]. The surface cleanliness was checked by Auger spectroscopy and O $1s$ photoemission. Photoemission experiments were carried out at room temperature in a VG ESCALAB II chamber in a pressure remaining better than of 5.10^{11} mbar during measurements. The $K\alpha_{3,4}$ contributions were eliminated by a standard numerical subtraction [12].

Before presenting the experimental data, let us summarize the main structural properties of the Ce/Fe(100) interface which will be published elsewhere [13]. The evolution of the Auger signals with the film thickness leads us to the conclusion that a two-dimensional growth occurs on the substrate maintained at room temperature without interdiffusion. This behaviour contrasts with the epitaxial growth observed at 750 K and the formation of a compound (close to Ce_2Fe_{17}) by reactive diffusion processes. Reflection–high-energy diffraction measurements indicate that the interfaces prepared at room temperature do not exhibit a long-range order. Although the interface is not long-range–ordered, the absence of interdiffusion and the two-dimensional growth mode allow to identify the Ce electronic configuration in each Ce layer in this system.

In fig. 1, we report the Ce $3d$ photoemission spectra for several coverages. These spectra exhibit a very complex structure reflecting the localized character of the $4f$ states and their hybridization with conduction electrons. The electronic properties of cerium result from the interplay between the intra-atomic $4f$ correlations, which tend to impose an integer number of f electrons, and the hybridization strength which induces a mixing of different $4f$ configurations. The ground state of metallic cerium-based compounds is usually a mixture of f^1 configuration with a small amount of f^0 configuration. This configuration admixture can be deduced from Ce $3d$ core level photoemission spectroscopy. The spectra of fig. 1 are dominated by a peak at $E = 369.6$ eV and its spin-orbit replicate at $E = 351$ eV. This structure corresponds to a final state of mainly $3d^9 4f^1$ character. Two weak satellites for each spin-orbit contribution appear at low and high energies and are associated with final states with mainly $3d^9 4f^0$ and $3d^9 4f^2$ character, respectively. The relative intensity of these satellites provides information on the electronic configuration of cerium atoms in the initial state. As demonstrated by Gunnarsson and Schönhammer [14], the high-energy structure ($4f^2$) reflects the hybridization in the final state between $3d^9 f^1$ and $3d^9 f^2$, whereas the low-energy structure ($4f^0$) is a measure of the configuration mixing ($4f^1$ and $4f^0$) in the initial state. For coverage smaller than one monolayer ($e \leq 1$ ML), the satellite intensities are very weak indicating that the hybridization and the interconfiguration mixing are not important. Cerium atoms are

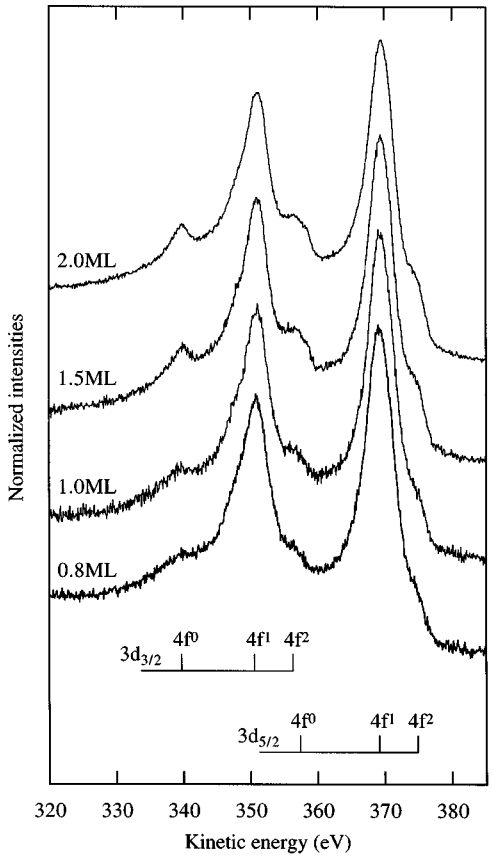

Fig. 1. – Ce 3*d* photoemission spectra for several coverages.

then nearly trivalent at the surface of Fe(100). On the other hand, the weight of these two satellites significantly increases for larger thicknesses suggesting that the electronic parameters (hybridization strength and interconfiguration mixing) are modified with increasing the film thickness from 1 ML to 2 ML. Nevertheless, this piece of information is averaged over two layers and the electronic configuration is likely different in the two layers. This remark is based on the sensitivity of the cerium electronic configuration to the presence of a free surface demonstrated by several studies [6]-[8].

In order to separate the surface and "bulk" contributions, we have prepared the following system. First, we have evaporated 1 ML of cerium that we have covered by several layers of samarium. Samarium is a trivalent rare earth and its non-f electronic structure is very similar to that of cerium. Therefore, samarium overlayers will reproduce the effect of cerium on the first monolayer and obviously they do not contribute to the Ce-3d photoemission spectrum which then directly gives the interface ("bulk") contribution. The photoemission spectrum of one layer of cerium recovered by 3 layers of Sm is reported in fig. 2 and compared with one uncovered Ce monolayer. A strong enhancement of the $4f^0$ and $4f^2$ structures is clearly evidenced proving that the first layer of cerium deposited on Fe is highly hybridized and mixed valent when it is covered. We have checked that the electronic configuration of cerium does not depend on the thickness of the Sm coverage. This suggests that the effect of surface is definitely limited to the first monolayer.

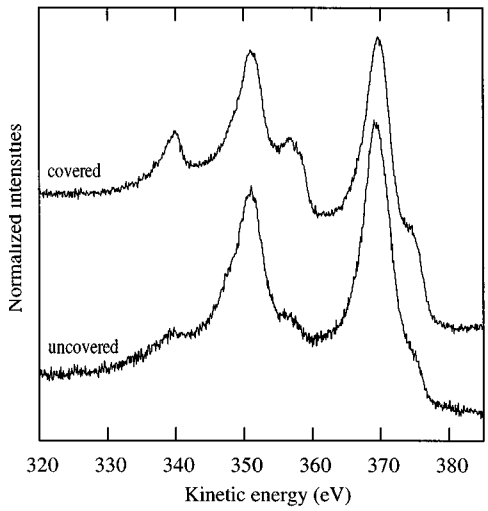

Fig. 2.

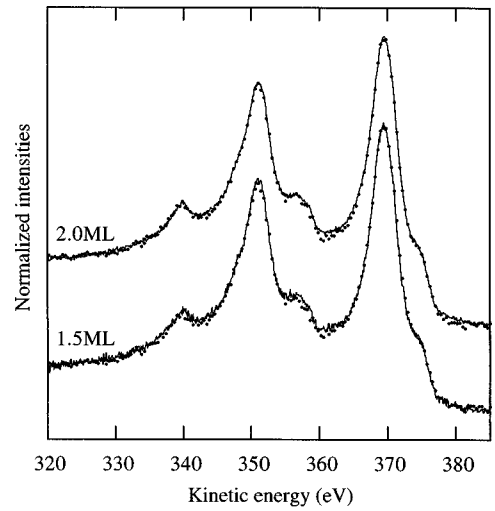

Fig. 3.

Fig. 2. – Ce 3d photoemission spectra of 1 ML of Ce (uncovered) and 1 ML of Ce covered by 3 ML of Sm (covered). The background are very different due to additional inelastic processes in the Sm layers.

Fig. 3. – Simulation of experimental spectra corresponding to 1.5 and 2 monolayers with the surface and interface contributions: the dots represent the experimental spectra and the solid lines are the reconstructed spectra (see text).

The photoemission spectra for film thicknesses larger than 1 ML have been simulated from two contributions: the interface spectrum determined as described above and corresponding to covered Ce atoms and a spectrum corresponding to trivalent configuration associated with the surface atoms. Then we try to simulate the background-subtracted 2 ML-spectrum $S_{2\,\mathrm{ML}}(\omega)$ from the surface spectrum $S_{\mathrm{SF}}(\omega)$ and the interface spectrum $S_{\mathrm{IF}}(\omega)$:

$$S_{2\,\mathrm{ML}}(\omega) = (1 + I_0)^{-1}\left[S_{\mathrm{SF}}(\omega) + I_0 S_{\mathrm{IF}}(\omega)\right]. \tag{1}$$

I_0 is an attenuation factor reflecting the fact that the photoelectron, resulting from a photoabsorption process in the interface layer, has to propagate through one Ce layer before escaping over the surface potential. The $(1 + I_0)^{-1}$ factor is a normalization factor (all background subtracted spectra have been normalized to one: $\int S_i(\omega)\mathrm{d}\omega = 1$ with $i = 2\,\mathrm{ML}$, SF and IF).

For intermediate coverages, we assume that covered cerium atoms are mixed valent whereas the surface ions are trivalent so that

$$S_{(1+x)\mathrm{ML}}(\omega) = (1 + x\,I_0)^{-1}\left[S_{\mathrm{SF}}(\omega) + x\,I_0 S_{\mathrm{IF}}(\omega)\right], \tag{2}$$

where x is the coverage ratio of the second layer ($0 \leq x \leq 1$).

Figure 3 shows the simulation of the experimental spectra corresponding to 1.5 ML and 2 ML according to relations (1) and (2). As the inelastic background is thickness dependent, we first remove a Shirley-type background from the surface and interface spectra by using the iterative method described in ref. [12]. Secondly, we calculate the spectrum with relations (1) and (2) and finally we add an inelastic background (Shirley-type) in order to compare with the experimental spectra. I_0 is considered as an adjustable in fig. 3. I_0 is found to be 0.6 but the result is weakly dependent on the I_0 value. This value corresponds to a mean free path $\lambda = 5.4$ Å.

Let us summarize the main results we have obtained. Cerium atoms deposited on Fe(100) exhibits a valence change with increasing Ce coverage. For low coverages (from isolated atoms to one monolayer), hybridization strength with iron atoms is insufficient to introduce a significant modification of the $4f$ electron configuration. Then the occupation number n_f remains nearly one until the completion of the first monolayer is reached. For larger coverages, a valence change occurs: if cerium atoms are covered by cerium (or samarium), n_f suddenly drops and the Ce electronic state becomes a mixing of $4f^1$ and $4f^0$ configurations. On the other hand, the cerium configuration for uncovered or surface atoms remain $4f^1$. The experimental data prove that the effect of surface is limited to the first layer since the $3d$ spectra of the interface layer does not depend on the thickness of the Sm film [13].

This valence change can be interpreted in the framework of the single-impurity Anderson model. In this model, the mixing between different $4f$ electronic configurations (essentially $4f^1$ and $4f^0$) is determined by the charge fluctuations energies (ε_f and U) and the hybridization strength (Δ) between $4f$ and conduction states. In core level photoemission, the energy separation between the different $4f$ configurations are changed in the final state by the Coulomb interaction (U_{fc}) between the core hole and the f states. The initial-state parameters are surely modified at the surface: the number of nearest neighbours is reduced leading to a reduction of the hybridization strength. Moreover, several studies have demonstrated that ε_f decreases at the surface stabilizing the f^1 configuration [15], [16]. The expected modification of the electronic configuration of cerium at the interface is actually observed. In the low-coverage regime (≤ 1 ML), the cerium atoms mainly hybridize with the Fe $3d$ states but remain trivalent. Between 1 and 2 ML, some Ce atoms of the interface are covered, the $4f$ energy increases, the mean hybridization strength increases due to additional interlayer Ce-Ce hybridization yielding a configuration change. This is illustrated in the insert of fig. 4 where we report the calculated intensity of the $4f^0$ satellite, which represents the configuration mixing in the initial

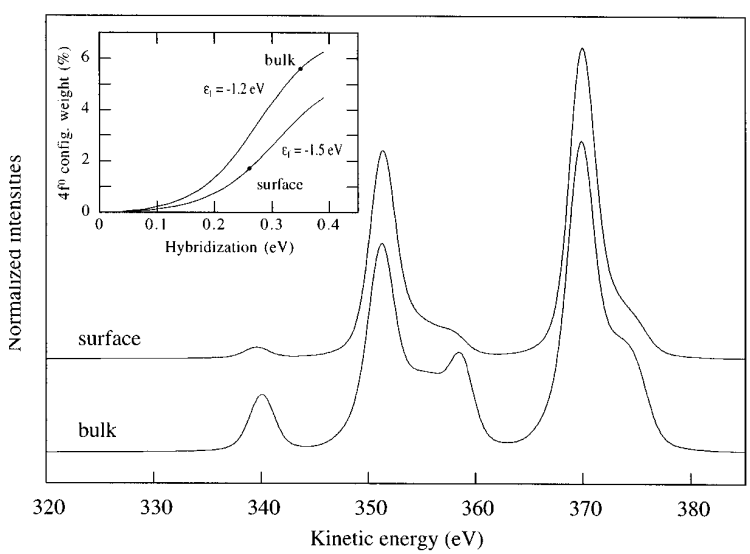

Fig. 4. – Photoemission spectra calculated in the framework of the Gunnarsson-Schönammer model. The parameters are $U = 9.6$ eV, $U_{fc} = 10.6$ eV; $\varepsilon_f = 1.2$ eV, $\Delta = 0.355$ eV for the surface. Inset: Calculated intensity of the f^0 structure as a function of the hybridization strength for $\varepsilon_f = 1.5$ eV and $\varepsilon_f = 1.2$ eV. The two dots represent the parameters used in the calculation of "bulk" and surface spectra.

state, as a function of hybridization for two values of ε_f (1.5 and 1.2 eV estimated for the surface and "bulk", respectively). The calculated photoemission spectra corresponding to the interface ("bulk") and surface spectra are reported in fig. 4. A qualitative agreement with the experimental spectra in fig. 1 is obtained. We would like to stress that a significant increase in the $4f^0$ structure intensity (factor 8) can be obtained with a relatively weak change of the electronic parameters ($\delta\varepsilon_f/\varepsilon_f = 0.25$ and surface hybridization is reduced by a factor 1.35 with respect to the bulk value). This behaviour is due to the strong non-linearity of the hybridization dependence of the $4f^0$ weight and configuration mixing in the Gunnarsson-Schönhammer approach (insert of fig. 4).

To conclude, we have observed a modification of the Ce electronic configuration at the Ce/Fe(100) interface. In the very low-coverage regime, cerium is trivalent whereas a mixed valent state is observed for higher film thicknesses. Thanks to an original method (deposition of an Sm film which simulates the surface without contributing to the experimental spectra) we unambiguously determine the "bulk" and surface signals. We demonstrate that the electronic configuration of cerium atoms at the interface with Fe suddenly changes when Ce atoms are recovered. This behaviour can be understood in the framework of the single-impurity Anderson model. Small variations of the electronic parameters (ε_f and Δ), when interface atoms are recovered, lead to a notable modification of the interconfiguration mixing. Surface effects, which we demonstrate to be limited to the first layer, appear to be due to the high sensitivity of the $4f$ configuration to small variations of the electronic parameters.

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