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LETTER TO THE EDITOR

Epitaxy of a mixed-valence Fe-Ce compound on Fe(100)

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Abstract. The growth mode, electronic structure and structural properties of the Ce/Fe(100) interface have been investigated by Auger spectroscopy, XPS and RHEED experiments. At 650 °C, an epitaxial Ce_xFe_y compound is formed. The surface lattice is of square symmetry, within the limit of experimental error, with a parameter $a_s = 4.05 \pm 0.15$ Å. This compound is found to be in a mixed-valence state, with a stoichiometry close to Ce_2Fe_{17} . Modifying the detection angle in order to increase surface sensitivity, XPS spectrum analysis shows a γ -like Ce-enriched surface. At room temperature, Ce grows in a disordered phase without interdiffusion.

Cerium metal is a fascinating element, which has been the subject of numerous theoretical and experimental studies since the beginning of this century. This interest can be easily understood in view of the fact that under pressure, temperature and/or alloying, the 4f electron of cerium can mix strongly with the conduction electrons, yielding the formation of highly correlated systems (Kondo-like, heavy-fermion and mixed-valence compounds (the so-called α -type compounds)). For instance, in the case of intermetallic systems with d-like metals [1, 2] or in the α -Ce phase [3, 4], the 4f electrons are so strongly hybridized with the conduction electrons (5d, 3d, etc) that the occupancy number of the 4f states (n_f) goes well below unity (≈ 0.7). This is precisely what we call a mixed-valence state, where the 4f electrons form a 'broad' 4f band whose width may be in the electron volt range. As expected, the formation of this 4f band, near the Fermi energy, is strongly dependent on the local environment of the cerium atoms in any given material.

The physical properties of such materials are obviously strongly related to the presence of these 4f 'delocalized' states near the Fermi level, especially the electrical and magnetic properties. In the last decade, several interesting applications of such unusual properties have been mentioned, essentially those related to surface properties such as for instance the catalytic activity [5]. Another area of interest (much more fundamental at this moment) is related to the magnetic properties of such materials, especially if we remember that some cerium intermetallics may be found in a ferromagnetic mixed-valence state (for instance $CeFe_2$ and $CeCo_5$ [6]). It has been shown theoretically [7] and more recently, from both neutron diffraction [8] and magnetic circular x-ray dichroism (MCD) experiments [9], that there is an ordered 4f magnetic moment on Ce in $CeFe_2$. Thus, it appears that in these cases Ce behaves like a transition element presenting *itinerant magnetism*. For both fundamental and practical reasons, it is thus really important to understand what are the relevant parameters that fix the valence of any rare-earth atom in a material and how the valence will behave at the surface (or interface). In particular, one of the goals is to

understand whether a true mixed-valence state could survive at the surface. This explains why numerous studies have been devoted, in the last few years, to the growth of rare-earth elements on d-like metal substrates [10, 11], special attention being given to the possible formation of an epitaxial compound at the interface [12]. In the case of Ce, several studies have been reported [13, 14]. In particular, Tang *et al* [15] have shown that depositions of Ce on Pt(111) lead, after annealing, to the growth of an epitaxial $\text{CePt}_{2,23}$ compound.

Recently, several interesting results have appeared concerning the Ce/Fe multilayer system [16]. Particularly, it was shown that Ce and Fe form sharp interfaces at room temperature (RT) (i.e. that there is no diffusion at RT). Moreover, from MCXD experiments, it was concluded that there exists, at RT, an unexpected ordered 5d magnetic moment on Ce in these multilayers. The Ce/Fe system is thus a good candidate for starting a study where the main interest lies in magnetic properties.

We report in this work structural and electronic properties of the Ce/Fe(100) interface formed at 650 °C. It is shown that an epitaxial Ce_xFe_y (probably $\text{Ce}_2\text{Fe}_{17}$) compound grows on top of Fe(100). The spectroscopic results (Auger electron spectroscopy (AES) and x-ray photoemission spectroscopy (XPS)) are presented and compared with those obtained for a polycrystalline CeFe_2 compound. We obtain the conclusion that this epitaxial compound is indeed in a mixed-valence state. We shall also mention here the growth mechanism of Ce films on Fe(100) at RT. More details about the interface formed at RT and for low Ce coverage ($< 20 \text{ \AA}$) will be given in a forthcoming paper.

Samples were prepared *in situ*, in a molecular beam epitaxy (MBE) chamber, by evaporating Ce onto an Fe(100) substrate held either at RT or at 650 °C. Ce was evaporated from a W crucible at a pressure of about 10^{-10} mbar after a careful outgassing of the crucible. Evaporation rates (in the range between 1 \AA min^{-1} and 5 \AA min^{-1}) and Ce thickness were measured with a water-cooled quartz microbalance leading to an error that can be estimated to 10%. In this work, we present the results obtained with Ce thicknesses lying between 0 and 30 Å.

Andrieu *et al* have shown [17] the possibility of obtaining Fe/Ir superlattices with Fe in the regular BCC phase. So, the Fe(100) substrates were prepared separately by growing 3500 Å of Fe on a 200 Å Ir buffer, which was evaporated onto an MgO(100) wafer at 650 °C. The Ir buffer is expected to improve the epitaxy and to stop O diffusion. The Fe film was covered by a 20 Å Ir layer to protect it against contamination. X-ray diffraction experiments were performed to check the good quality of the substrates. Before each Ce evaporation, the Fe substrate was cleaned by Ar ion bombardment at 450 °C and then heated for 10 min at 450 °C. Surface recrystallization was checked by reflection high-energy electron diffraction (RHEED) experiments and the presence of any impurities was monitored by AES. The polycrystalline CeFe_2 sample was obtained by arc melting. In order to obtain a clean surface it was scraped *in situ* with a diamond file and the cleanness was checked by AES.

Structural studies were performed by RHEED with a 20 keV electron beam under 1° or 2° incidence. The growth modes were determined by AES intensity measurements. Spectra were recorded in the derivative mode with a CMA spectrometer. The energy of the incident beam was set to 2 keV with a $2 \mu\text{A}$ emission current. XPS experiments were performed in a VG Escalab MKII apparatus connected to the MBE chamber. An Mg $K\alpha$ x-ray source was used and the spectra were recorded with a hemispherical analyser. The overall XPS resolution was about 1.1 eV. The base pressure in our apparatus was about 5×10^{-11} mbar, which was sufficient to keep a clean surface for 2 h.

In the following, we will discuss the results obtained for Ce depositions on a substrate held either at RT or at 60 °C. We report in figure 1(a) the Ce(NVV) and Fe(MVV) peak intensities and the intensity ratio $R = \text{Ce(NVV)}/\text{Fe(MVV)}$ for the early stages of the Ce

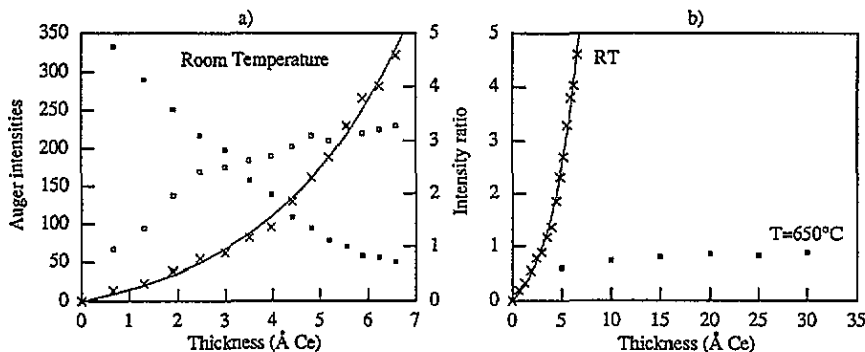


Figure 1. (a) Auger results obtained for the substrate at RT; we show the Fe(MVV) intensity (■) and the Ce(NVV) intensity (□). The intensity ratio Ce(NVV)/Fe(MVV) is also plotted (×) and has been fitted (full line) with $R = A(1 - \exp(-x/\lambda_{Ce}))/\exp(-x/\lambda_{Fe})$ with $\lambda_{Ce} = 4.3 \text{ \AA}$ and $\lambda_{Fe} = 3.9 \text{ \AA}$. (b) With the same scale, the intensity ratio Ce(NVV)/Fe(MVV) for Ce depositions on the Fe(100) face at RT (×) and 650 °C (■).

film growth on the Fe(100) substrate at RT. In figure 1(b), we present the intensity ratio R obtained for Ce depositions on the substrate at 650 °C and for Ce thickness lying between 0 and 30 Å (for comparison, the intensity ratio at room temperature is shown again on the same scale).

The Ce thicknesses given by the quartz microbalance have been calibrated assuming a layer-by-layer growth mode (as is shown below). Thus, the well defined break in the Ce(NVV) intensity (figure 1(a)) is supposed to correspond to the completion of one dense Ce monolayer. This assumption is supported by the values of electron mean free paths obtained by fitting the intensity ratio R in a layer-by-layer model (full line in figure 1(a) and (b)). In such a model, R is given by $R = A[1 - \exp(-x/\lambda_{Ce})]/\exp(-x/\lambda_{Fe})$ where x is the Ce thickness and λ_{Ce} and λ_{Fe} are the electron mean free paths at the Ce(NVV) and Fe(MVV) energies respectively. In accordance with commonly accepted values [18], λ_{Ce} and λ_{Fe} have been found to be 4.3 and 3.9 Å respectively.

We notice in figure 1(a) that the Fe(MVV) signal rapidly decreases with the Ce coverage: it is reduced by one order of magnitude for a Ce thickness of 7 Å. This behaviour strongly indicates that at RT a bidimensional Ce growth occurs without significant interdiffusion. Moreover Auger spectra recorded for a 50 Å Ce deposit at RT indicate the absence of any Fe(MVV) signal, ruling out the possibility of any significant interdiffusion at the interface. This result is an agreement with previous work on Ce/Fe multilayers made at low temperature [16], for which sharp interfaces were found. On the other hand, as is shown in figure 1(b), data obtained for Ce depositions at 650 °C deviate drastically from the intensity ratio curve obtained at room temperature. When the Ce thickness increases, the intensity ratio saturates rapidly, yielding the conclusion that Fe atoms are still present at the surface. This behaviour allows us to rule out the possibility of the formation of scattered Ce islands on the Fe(100) surface (this will be confirmed later by RHEED experiments) and leads us to the conclusion that, at 650 °C, Ce and Fe interdiffuse at the interface and form probably an intermetallic Ce_xFe_y alloy (or compound). We show in figure 2 the RHEED patterns obtained for a 30 Å Ce deposit on Fe(100) at 650 °C and annealed at 650 °C for 10 min. These streaked patterns, which are obtained for all thicknesses between 10 and 30 Å, indicate a bidimensional ordered growth. Considering the Auger results, this strongly suggests the formation of an epitaxial Ce_xFe_y compound on the Fe(100) substrate.

These patterns correspond to $(\sqrt{2} \times \sqrt{2})$ R 45° structure with respect to the mesh of the Fe(100) plane, leading to an in-plane structure of square symmetry with a parameter of 4.05 ± 0.15 Å. For Ce thicknesses larger than 30 Å, the RHEED patterns rapidly become diffuse, indicating that epitaxy is lost. RHEED experiments were also carried out on Ce films evaporated on the Fe substrate held at RT. For 20 and 50 Å Ce deposits, the RHEED patterns show identical diffuse background, indicating the growth of a disordered Ce phase. This is consistent with the results reported for the Ce/Fe multilayers, where Ce was found to be amorphous for thicknesses less than 70 Å. Information concerning the stoichiometry of this compound have been obtained by Auger spectroscopy and XPS measurements on Ce 4d core levels. We show in figure 3(b) the spectra in the vicinity of the Ce 4d emission. The structure at 1162.7 eV is due to the Fe 3s core level. By comparing the Fe 3s intensities between the normalized spectra of the polycrystalline CeFe₂ sample and the Ce_xFe_y epitaxial compound, we can unambiguously rule out the possibility of formation of a Ce-Fe phase of stoichiometry close to CeFe₂. By measuring the Ce(NVV)/Fe(MVV) Auger intensity ratios on the CeFe₂ polycrystalline sample and on the epitaxial compound, it is possible to calculate the Ce concentration for the epitaxial compound. These intensity ratios are found to be 2.74 and 0.85 for CeFe₂ and the Ce_xFe_y epitaxial compound respectively. For the epitaxial compound, this corresponds to a Ce concentration close to 0.13. In addition, the Ce 4d spectrum, recorded for a detection angle of 50° from the sample normal (upper curve in figure 3(b)), clearly shows an enhancement of the Ce signal with respect to the Fe 3s signal, indicating a Ce-enriched surface. Due to the small electron mean free path for Ce(NVV) and Fe(MVV) Auger transitions (located at 80 eV and 47 eV respectively), the sample surface strongly contributes to the Auger signal. Thus, considering the presence of a Ce-enriched surface, the concentration value of 0.13 could not be representative of the bulk Ce concentration, which must be less than this value. This strongly suggests a stoichiometry close to Ce₂Fe₁₇ (for which the Ce concentration is 0.10) for the epitaxial Ce_xFe_y compound formed on the Fe(100) face. Moreover two structure types have been reported for the Ce₂Fe₁₇ compound: Th₂Zn₁₇ type and Ni₁₇Th₂ type [19] for which a rectangular symmetry plane exists with a mesh of 4.00×4.14 Å². This is a (110) plane constituted of Fe atoms. Considering the RHEED results on our epitaxial compound, leading to a square plane of parameter 4.05×0.15 Å², the commensurate epitaxy of a strained phase close to Ce₂Fe₁₇ on the Fe(100) face is suggested.

We have investigated the electronic structure of this epitaxial Ce_xFe_y compound by XPS experiments on the Ce 3d and Ce 4d core levels. We want here to focus mainly on the Ce valence state. Many studies on Ce-based intermetallic compounds, such as for instance CeNi₅, CeNi₂ or CePd₃ [1], have shown that Ce 3d and Ce 4d spectra are very sensitive to the Ce valence state and thus to the hybridization strength between the 4f and conduction states. We present in figure 3 the XPS spectra recorded for a 30 Å Ce deposit at 650 °C and the results obtained for the polycrystalline CeFe₂ sample. Both Ce 3d spectra (figure 3(a)) are very similar and exhibit, for each spin-orbit component 3d_{3/2} and 3d_{5/2}, three features assigned to the three different screening channels 4f⁰, 4f¹ and 4f². It is well known [1] that the 4f² component, due to a 'shake-down' final-state effect, can be directly related to the hybridization. Moreover, the mixed-valence state is unambiguously revealed by the presence of structures assigned to the 4f⁰ screening channel. This leads us to conclude that the epitaxial Ce_xFe_y compound is in a mixed-valence state for which the 4f states are strongly hybridized with the conduction states. This conclusion is supported by the XPS Ce 4d results (figure 3(b)), which exhibit the two structures assigned to the (4d_{3/2}-4d_{5/2}) spin-orbit doublet of the 4f⁰ channel at 1132.2 eV and 1135.6 eV respectively. We present also in figure 3 XPS spectra recorded with a detection angle of 50° from the sample normal,

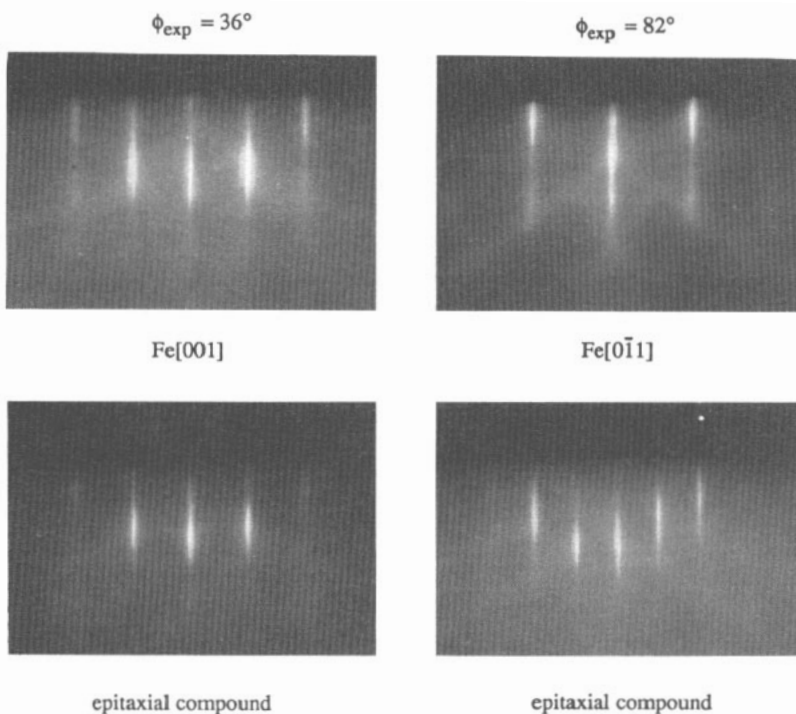


Figure 2. RHEED patterns with the electron beam incident along the Fe[001] and Fe[0 $\bar{1}$ 1] directions obtained on the Fe(100) substrate and on the epitaxial compound.

increasing the surface sensitivity. Both Ce 3d and Ce 4d spectra exhibit a decrease of the $4f^0$ component, indicating a γ -like valence state surface. This is supported by the broadening of the Ce 3d $_{3/2}$ and Ce 3d $_{5/2}$ features, which could be due to the superposition of shifted bulk and surface contributions [20].

In conclusion, the Ce/Fe(100) interface has been studied at room temperature and at 650 °C by structural and spectroscopic experiments. We have shown that two different behaviours occur. At RT, a disordered Ce phase grows without interdiffusion. On the other hand, at 650 °C Ce and Fe intermix at the interface to form a Ce $_x$ Fe $_y$ compound in commensurate epitaxy on the Fe(100) face up to 30 Å Ce deposited. This epitaxial Ce-Fe intermetallic is a strongly hybridized mixed-valence compound with a trivalent Ce-enriched surface. Moreover, the structural results and the bulk Ce concentration (which is found to be less than 0.13) strongly suggest that this epitaxial compound could be the Ce $_2$ Fe $_{17}$ phase. In order to obtain more precise information concerning the structure, extended x-ray absorption fine structure and x-ray diffraction experiments are now under investigation. The main interest in the formation of this epitaxial Ce-based compound on top of Fe(100) is related to its magnetic properties. The next step in our study will thus be to investigate by MCXD the local magnetic properties of Ce atoms in this epitaxial compound. In particular, the existence of a 4f magnetic moment and its temperature dependence has to be considered.

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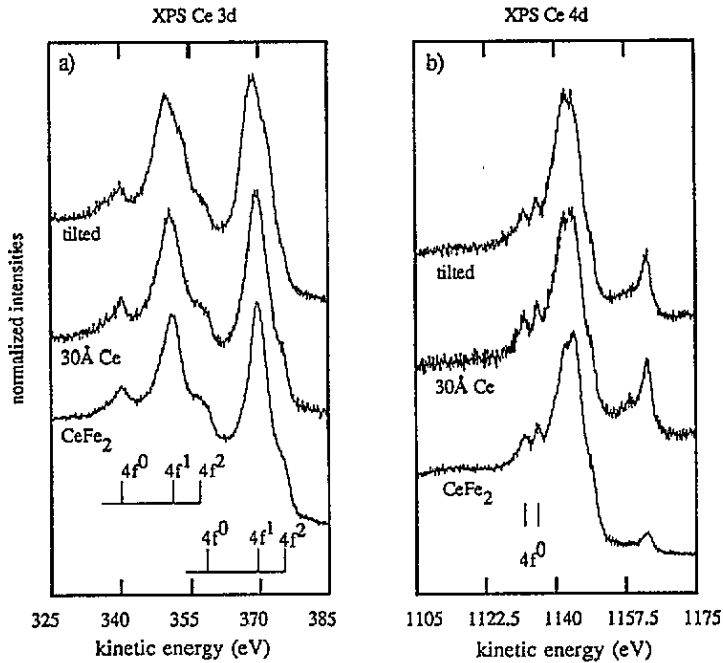


Figure 3. Ce 3d and 4d XPS spectra ((a) and (b) respectively) for the CeFe₂ polycrystalline sample (lower curves) and for a 30 Å Ce epitaxial compound recorded with normal detection (middle curves) and with a detection angle of 50° from normal (upper curves).

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