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Journal of Electron Spectroscopy and Related Phenomena xxx (2005) xxx–xxx

**JOURNAL OF
ELECTRON SPECTROSCOPY**
and Related Phenomena

www.elsevier.com/locate/elspec

XPS study of Eu(III) coordination compounds: Core levels binding energies in solid mixed-oxo-compounds $\text{Eu}_m\text{X}_x\text{O}_y$

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Received 23 November 2004; received in revised form 10 August 2005; accepted 19 August 2005

Abstract

Literature is relatively sparse on XPS studies of europium compounds: it is essentially restricted to metallic compounds (EuM_5 , in which M is a transition metal) or to simple oxides. While particular interest have been devoted to understanding physical phenomenon in the beginning of “shake-down” and “shake-up” satellites evidenced on core-level regions of the lanthanides, few information on absolute binding energies (BE) was available. This paper reports an XPS binding energy data base for europium(III) compounds, in which Eu cation have various chemical environments: simple oxide Eu_2O_3 , Eu mixed oxides with organic oxalate, acetylacetonate or inorganic sulfate, nitrate, carbonate ligands. The values of core-level BE (O_{1s} , Eu_{3d} and Eu_{4d}) and the characteristics of shake-down satellites of Eu_{3d} are reported, and their variations are attributed to ionicity/covalency changes. Such interpretation was already published for Group A mixed oxides and zeolites. These data are needed for determining Eu(III) species sorbed onto minerals in the presence of various ligands in the framework of retention studies for assessing the safety of future nuclear waste disposals.

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Keywords: XPS; Europium(III) compounds; Binding energy; Ionicity; “Shake-down” satellite

1. Introduction

Understanding the chemistry of trivalent f-block elements is important for managing nuclear wastes. Indeed, isotopes of lanthanides are fission products of uranium-235 and trivalent actinides (mainly Am and Cm isotopes) are activation products of uranium-238. Lanthanides are also studied as non-radioactive analogues of trivalent actinides. In order to understand the chemical behaviour of these elements in geological context for future nuclear waste storage, it is needed to understand their interaction mechanisms with natural solids such as oxides or clays. Chemical retention, i.e. partition of the metallic element between aqueous solution and mineral surface, is a key phenomenon for assessing the safety of possible nuclear waste disposal.

We are studying interaction mechanisms between an aqueous Eu(III) and an alumina surface, in the presence of an inorganic or organic complexing agents [1]. Our approach is based on the combination of spectroscopic methods as X-ray photoelectron spectroscopy (XPS), and sorption experimental data interpreted with thermodynamic.

Many XPS studies are published on Group A or transition metals oxides [2]; while much less XPS studies have been published on lanthanides compounds, those on Eu(III) compounds are particularly sparse.

Numerous XPS data reported in the literature on mixed oxo-compounds suffer from a lack of information concerning O_{1s} results. Typically, no O_{1s} values were reported in refs. [3,4], while M and/or X core level photoelectron peaks BE were reported for several $\text{M}_m\text{X}_x\text{O}_y$ oxocompounds—M is a metallic cation and the most electropositive atom, and X an heteroatom such as, e.g. C, N, S, Si, P. However, Barr published this information for silicas, zeolites, clays, aluminas and aluminates [5–7], to our knowledge, these are the only studies report-

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ing detailed O_{1s} data and interpretation for series of different oxocompounds.

For this reason, we attempted to study the O_{1s} signal in the present work, however this is in principle virtually impossible for sorption on alumina, since the O_{1s} BE of alumina can not be distinguished from those of the oxocompounds that we aim to study.

The XPS studies on lanthanides have been specially focused on the research for the origin of “shake-down” and “shake-up” satellites in 3d and 4d core-level regions. When lanthanide ions compounds are analyzed by XPS, unoccupied 4f-subshells are lowered in energy by the potential of the photohole (Coulomb interaction of the created photohole with the electronic system), which allows a conduction electron to occupy these 4f-subshells; this increases the occupation of 4f-subshells, corresponding to an apparent change of the initial valence of the lanthanide cation [8–12]. With increasing atomic number and thereby increasing 4f occupation, the probability of this mechanism decreases, it approaches zero in Sm systems [13]. In europium compounds, however, due to the energetic degeneracy of the $4f^65d^1$ and $4f^75d^0$ configurations, both configurations are observed in the final-state, whatever the initial valence state [11].

This apparent change of the initial valence has been observed for different rare-earth systems: Gd core levels in GdF_3 [14], core levels of La oxocompounds [15], and in some binary and mixed oxides of La and Ce elements [15]. Several authors published XPS studies of various metal oxides, including rare-earth oxides: CeO_2 , TbO_2 , La_2O_3 and Tb_2O_3 [16–19].

Eu_{3d} core-level XPS spectra of $EuAg_5$, $EuPd_2P_2$ and $EuCu_5$ are reported to show two peaks corresponding to a rearrangement of the 4f-subshells electronic occupation after photoionization; in these compounds europium is exclusively divalent as indicated by Mössbauer spectroscopy and magnetic susceptibility measurements [8–12]. One peak corresponds to the initial divalent $5d^04f^7$ configuration of Eu(II) (main peak) and the other peak at about 6.5–8.0 eV higher BE is attributed to the $5d^14f^6$ configuration corresponding to an excited state of Eu(II) in which the 4f rearrangement results in an apparent “Eu(III) configuration”, i.e. the so-called shake-up satellite in the XPS spectrum, the intensity of the satellite is about 15% of the main peak [9,11,12]. Besides this shake-up process observed for Eu(II) compounds, the shake-down reverse process have been observed for Eu(III) compounds: their XPS spectra can show a satellite at BE lower than the photoelectron peak in the 3d and 4d regions of europium. Burroughs et al. [20] have proposed that beside electrostatic coupling between the core hole and the 4f electrons, these satellite peaks in the spectra would also be originated in charge transfer coexcitations, principally from O_{2p} to lanthanide $_{4f}$ for lanthanide having a partly occupied 4f-subshell. Whatever their physical origins, these satellites make it virtually impossible to estimate the degree of valence mixing from XPS studies of the corresponding lanthanide compounds.

The relative intensities of the photoelectron satellites vary as compared to those of the corresponding main peaks of Eu(II) and Eu(III), and the probability for the presence of shake-up and shake-down processes seems to be correlated with the chemical environment of europium ion [21]. From XPS spectra

of the $Eu_{3d5/2}$ and Eu_{4d} core-level regions in Eu(III) compounds ($EuRh_5$, $EuNi_5$, $EuPt_5$ and $EuPd_5$) Laubschat et al. have found, that the contribution of the divalent final-state component increases with increasing the atomic number within a same column of the Periodic Table. This effect is present to a lesser extent in the Eu_{4d} regions as well. Unfortunately, this corresponds to the influence of Eu(III) chemical environment on satellite intensity.

In literature, much attention has been devoted to the energy separations between the satellite and main photoelectron peaks, while less attention have been paid to absolute binding energies. In a systematic study of 600 compounds containing 77 elements [22], Jorgensen and Berthou measured absolute binding energies of the inner and outer shells of rare earth elements and ligands in various rare earth compounds. They corrected charge-up shifts for non-conducting materials by using the C_{1s} peak from mounting tape. However, use of this calibration method is unsatisfactory. Indeed, the C_{1s} BE of mounting tape, a non-conducting material, is equally a function of charge-up shifts of studied material. Therefore, the BE values estimated by Jorgensen and Berthou are associated with quite large uncertainties.

Uwamino et al. [23] have also studied a variety of rare-earth compounds (oxides, sulfates and oxalates) by XPS, and the BE values they reported also suffer from an energy calibration problem of the XPS spectra: they used a thin gold layer deposited on each surface and calibration of all the photoelectron peaks BE relative to that of $Au_{4f7/2}$ at 83.3 eV, which neglects the insulating character of the analysed surfaces, and assumes the gold was layer homogeneous.

In the present paper, the following Eu(III) compounds have been studied by XPS: Eu_2O_3 , $Eu_2(SO_4)_3$, $Eu_2(CO_3)_3$, $Eu(\text{acetylacetonate})_3$, $Eu(NO)_3$ and $Eu_2(C_2O_4)_3$. They are relevant of chemical species sorbed onto an alumina surface in the presence of complexing agents, studies that we report elsewhere [1]. The BE values of core level photoelectron peaks of oxygen (O_{1s}), europium (Eu_{3d} , Eu_{4d}) in Eu(III) compounds are given by using contamination carbon signal at 284.6 eV for energy calibration, and then discussed. Moreover, the characteristics of “shake-down” satellites of $Eu_{3d5/2}$ and Eu_{4d} are presented in terms of intensity relative to the parent photoelectron peak and of BE positions. To our knowledge, this combination of information from main photoelectron peaks and satellites has not been considered in the literature. The values of core-level BE and the characteristics of shake-down satellites of Eu_{3d} and Eu_{4d} are reported and explanation of BE evolution in terms of ionicity/covalency changes is proposed supported by numerous results available in the literature on Group A mixed oxides [2].

2. Experimental procedures

2.1. Samples

Commercial products from Aldrich® were used as standard samples containing europium in oxidation state (III): Eu_2O_3 (99.999% purity), $Eu_2(C_2O_4)_3$ (Eu(III) oxalate hydrate of 99.9% purity), $Eu(\text{acac})_3$ (Eu(III) acetylacetonate hydrate of 99.9% purity), $Eu_2(CO_3)_3$ (Eu(III) carbonate hydrate of 99.9%

purity), $\text{Eu}_2(\text{SO}_4)_3$ (Eu(III) sulfate hydrate of 99.9% purity) and $\text{Eu}(\text{NO}_3)_3$ (Eu(III) nitrate hydrate of 99.99% purity). Powders were pressed to obtain circular disks ~ 0.5 mm thick and 10 mm in diameter, then placed in an oven at 50°C for one day.

2.2. X-ray photoelectron spectroscopy (XPS)

Experiments were carried out using a VG Escalab MKII spectrometer with an unmonochromated Al $K\alpha$ ($h\nu = 1486.6$ eV) radiation. The source characteristics were of 10 kV and of 5 mA. The pressure was lower than 10^{-8} Pa in the analysis chamber. The photoelectrons emitted from the ionization of target atoms were selected in kinetic energy by passing through an analyzer and the collected signal was amplified by five Channeltron detectors, which permits lower detection limits: down to 1 or even 0.1 at%. Depending on the core level investigated, the depth probed by XPS could be as large as 5 nm.

A freshly abraded silver sample was used for standardizing the BEs of the spectrometer on the well-known $\text{Ag}_{3d_{3/2}}$ and $\text{Ag}_{3d_{5/2}}$ XPS transitions at 374.3 and 368.3 eV, respectively.

The BE positions of O_{1s} , $\text{Eu}_{3d_{5/2}}$ (the more intense of the two Eu_{3d} photoelectron peaks) and Eu_{4d} have been determined for all the above Eu(III) compound. The O_{1s} signal of Eu(III) compounds is included in the global O_{1s} signal obtained mainly from alumina (see Section 1): we analyzed the global signal, since decomposing it for extracting its Eu component was virtually impossible or not reliable. Although the Eu_{4d} signal is less intense than the Eu_{3d} one, it is interesting to use both peaks, since their great difference in BEs allows to evidence depth heterogeneities of the samples. Moreover, the intensities and BE positions of “shake-down” satellites of $\text{Eu}_{3d_{5/2}}$ and Eu_{4d} can probe the chemical environment of Eu(III). The accuracy of the measured BE values was estimated to be equal to ± 0.3 eV.

As charging effects are unavoidable in the XPS study of our insulating samples, the BE was calibrated with contamination carbon in each sample. For this internal reference, we used the C_{1s} level of saturated hydrocarbons at 284.6 eV.

3. Results and discussion

In the following section, we report and discuss the influence of the chemical environment of Eu(III) on BE values for core-level photoelectron peaks O_{1s} , $\text{Eu}_{3d_{5/2}}$ and Eu_{4d} , and on the “shake-down” satellites of $\text{Eu}_{3d_{5/2}}$ and Eu_{4d} .

3.1. O_{1s} peak

Our measured BE values of the O_{1s} signals for the Eu(III) compounds (Table 1) were all found in the 524–538 eV XPS range (Fig. 1). The shape of the O_{1s} signal is quite different for Eu_2O_3 , when compared to the other Eu(III) compounds: for Eu_2O_3 an intense peak was found at high BE (531.1 eV) and a shoulder at lower BE (529.0 eV), whereas for the other compounds a single peak was observed for each Eu(III) compound in the range 531.2 eV for $\text{Eu}_2(\text{C}_2\text{O}_4)_3$ to 533.5 eV for $\text{Eu}(\text{NO}_3)_3$.

Our results are consistent with those of Barr [5–7,24] on zeolites. He has evidenced that the mixing of $x\text{SiO}_2$ and $y\text{NaAlO}_2$

Table 1

BE values of O_{1s} photoelectron peak in Eu(III) compounds (BE values are corrected from contamination carbon at 284.6 eV)

Eu(III) compound	BE of O_{1s} (in eV)
Eu_2O_3	531.1/529.0
$\text{Eu}_2(\text{C}_2\text{O}_4)_3$	531.2
$\text{Eu}(\text{acac})_3$	531.2
$\text{Eu}_2(\text{CO}_3)_3$	531.7
$\text{Eu}_2(\text{SO}_4)_3$	531.9
$\text{Eu}(\text{NO}_3)_3$	533.5

to form various zeolites is associated with significant changes in the O_{1s} signals – shape and BE – consistently tracking the x/y ratio, suggesting that the Si–O and Al–O bonds are altered in zeolites as compared to the simple oxides SiO_2 and NaAlO_2 . He has interpreted the single peak of relatively narrow width as evidence that this alteration results in a single type of oxygen whereas two different peaks are observed for the two simple oxides SiO_2 and NaAlO_2 .

For Eu_2O_3 , the peak located at high BE may be attributed to water adsorbed during the formation of the pellet (adsorbed OH implying $\text{Eu}(\text{OH})_3$ compound) following Burroughs et al. [20] who proposed this interpretation for similar peaks of high binding energy in the O_{1s} spectra of rare-earth oxides, since they disappeared on heating samples at 1000°C for 1 h in vacuum. Similarly, Hammond et al. [25] have obtained spectra of CdO Oxide with two peaks in the O_{1s} signal (530.7 and 528.6 eV), and they have attributed the peak at higher BE to $\text{Cd}(\text{OH})_2$, since this peak totally disappeared on heating the surface at 300°C for 1 h, whereas the lower BE peak persisted.

The nature of Eu(III) compounds influences the BE of the O_{1s} photoelectron peak (difference between the simple oxide Eu_2O_3 and complex oxides), their BEs increases as follows (Table 1 and Fig. 1):

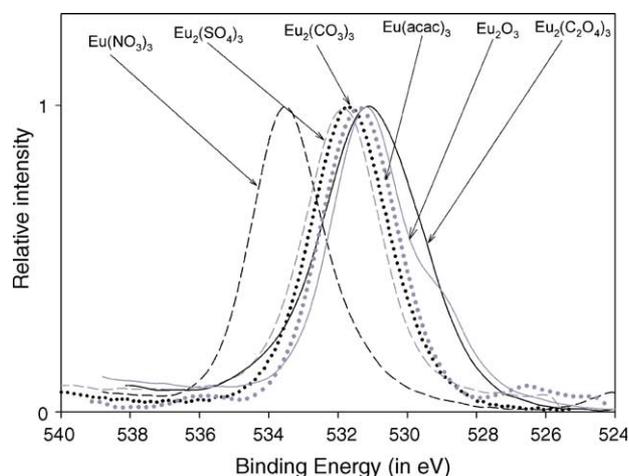
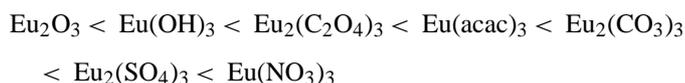


Fig. 1. O_{1s} XPS region as a function of Eu(III) compounds.

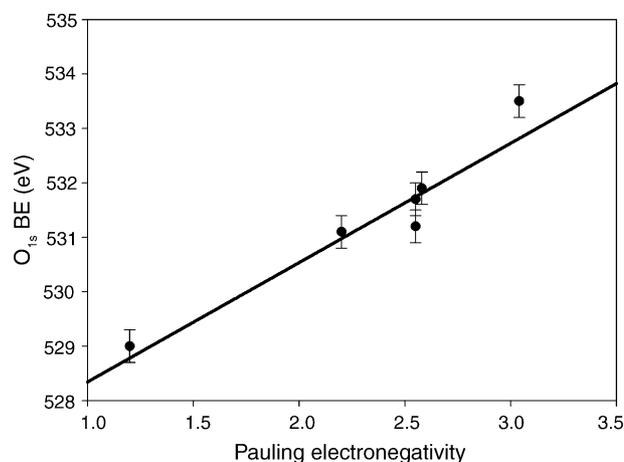


Fig. 2. Correlation between Pauling electronegativity of heteroatom X and O_{1s} BE value for Eu(III) compounds ($r^2 = 0.894$; $BE = (526.2 \pm 0.8) + (2.2 \pm 0.3) \times \text{electronegativity}$).

The trend in this series is correlated to the electronegativity of heteroatom X in $Eu_mX_xO_y$; since the respective Pauling electronegativities of Eu, H, C, S and N [28] increase in the following order:

$$Eu(1.2) < H(2.2) < C(2.55) < S(2.58) < N(3.04)$$

where $X = Eu$ for Eu_2O_3 . The correlation is even reasonably linear (Fig. 2). Using the O_{1s} photoelectron peak allowed to discriminate: (1) Eu_2O_3 from other Eu(III) compounds; (2) the nature of the complexing agent – carbonate, organic, sulfate or nitrate ligands – of Eu(III), excepted when oxalate and acetylacetonate were simultaneously present. From considerations based on electronegativity changes of the heteroatom, it might very well be feasible to predict BE values for other Eu(III) compounds, including those that are expected to be present on alumina surfaces.

A usual explanation is: more electronegative the heteroatom is, the more ionic the Eu–O bond is and the higher the BE values of O are. Similarly, Barr [5–7] has typically evidenced on various zeolites, that the O_{1s} BE values increase from $O_{1s} = 529.9$ eV for $NaAlO_2$ the more ionic compound, to $O_{1s} = 532.7$ eV for SiO_2 the more covalent compound in a series of mixed $(SiO_2)_x(NaAlO_2)_y$ compounds. The values of the O_{1s} BE increase with x for various zeolites. The O_{1s} BE increasing shift is correlated to this increasing degree of covalency in the zeolite lattice. This could also explain the observations of Shoen [26], who proposed a BE of 529.2 eV in Ag_2O , while Hammond et al. [27] proposed a value of 530.6 eV in Ag_2CO_3 : the C–O bond is more covalent than the M–O bond.

3.2. Eu_{3d} and Eu_{4d} peaks

$Eu_{3d_{5/2}}$ BE values have been obtained for several Eu(III) compounds (Table 2) in the XPS range 1120–1145 eV (Fig. 3), while the Eu_{4d} BE values (Table 3) are in the XPS range 115–150 eV (Fig. 4).

Spectra of lanthanides with an incompletely occupied 4f-subshell exhibit splitting into two signals separated. This was

Table 2

BE values of $Eu_{3d_{5/2}}$ photoelectron peak, of its associated shake-down satellite and ratio of their intensities in Eu(III) compounds (BE values are corrected from contamination carbon at 284.6 eV)

Nature of Eu(III) compound	BE of $Eu_{3d_{5/2}}$ (in eV)	BE of shake-down satellite of $Eu_{3d_{5/2}}$ (in eV)
Eu_2O_3	1133.7	1123.5
$Eu_2(C_2O_4)_3$	1133.9	1124.0
$Eu(acac)_3$	1135.0	1124.9
$Eu_2(CO_3)_3$	1135.3	1125.2
$Eu_2(SO_4)_3$	1135.9	1125.7
$Eu(NO_3)_3$	1136.4	1126.0

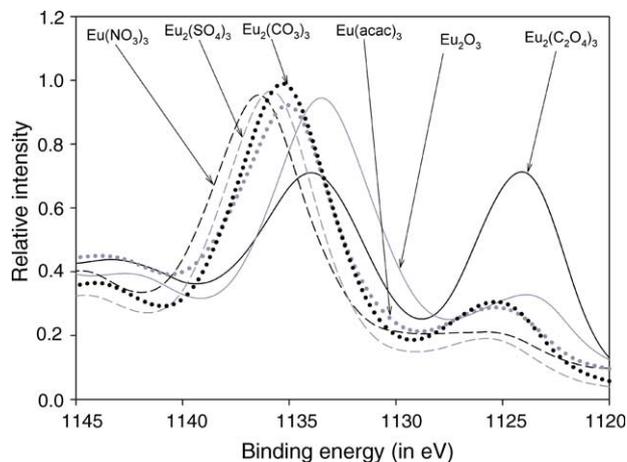


Fig. 3. $Eu_{3d_{5/2}}$ XPS region as a function of Eu(III) compounds.

Table 3

BE values of Eu_{4d} photoelectron peak, of its associated shake-down satellite and ratio of their intensities in Eu(III) compounds (BE values are corrected from contamination carbon at 284.6 eV)

Nature of Eu(III) compound	BE of Eu_{4d} (in eV)	BE of shake-down satellite of Eu_{4d} (in eV)
Eu_2O_3	134.9	128.5
$Eu_2(C_2O_4)_3$	134.4	127.3
$Eu(acac)_3$	136.1	129.0
$Eu_2(CO_3)_3$	136.5	129.1
$Eu_2(SO_4)_3$	136.9	127.9
$Eu(NO_3)_3$	137.7	127.5

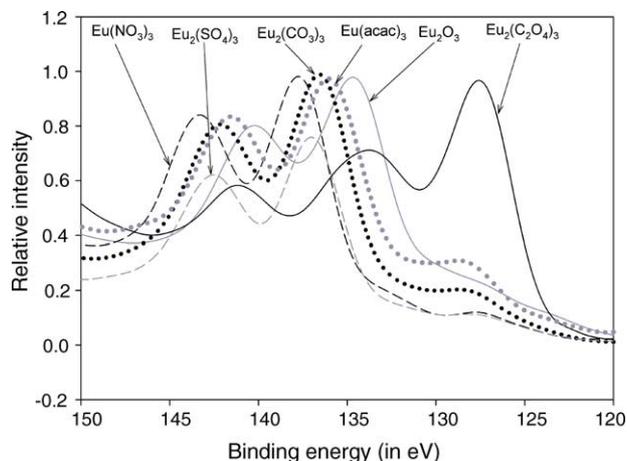
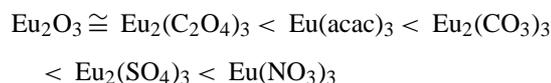


Fig. 4. Eu_{4d} XPS region as a function of Eu(III) compounds.

here observed from 7 to 10 eV for the Eu_{3d} and Eu_{4d} peaks of all the Eu(III) compounds. These 7–10 eV values are consistent with values published for oxides or Eu-transition metal compounds, and attributed to the main photoelectron peak of Eu(III) – highest BE – and its shake-down satellite, corresponding to an apparent change in the 4f-subshell occupation number similar to Eu(II), and located at a weaker BE than the main photoelectron peak [8–12]. The exploitation of these satellites for the determination of Eu(III) chemical environment is discussed below.

The $\text{Eu}_{3d5/2}$ BEs of Eu(III) compounds increase from 1133.5 eV for Eu_2O_3 to 1136.4 eV for $\text{Eu}(\text{NO}_3)_3$, according to the following sequence (Table 2 and Fig. 2):



The same trend was found for the Eu_{4d} peak (Table 3 and Fig. 4). Again, the nature of the Eu(III) compound has an influence on the BE values of Eu_{4d} , which varies from 134.4 eV for $\text{Eu}_2(\text{C}_2\text{O}_4)_3$ to 137.7 eV for $\text{Eu}(\text{NO}_3)_3$. As the same BE evolution between $\text{Eu}_{3d5/2}$ and Eu_{4d} is observed, no surface modification of samples occurred during the analysis of Eu(III) compounds.

The $\text{Eu}_{3d5/2}$ BE values were difficult to discriminate for $\text{Eu}_2(\text{SO}_4)_3$ and $\text{Eu}(\text{NO}_3)_3$, but a simultaneous analysis with those of Eu_{4d} allowed to discriminate between the two compounds. The same problem was encountered for discriminating between Eu_2O_3 and $\text{Eu}_2(\text{C}_2\text{O}_4)_3$, and the same evolution was successfully used.

The only data available in the literature for Eu_2O_3 are those of Schneider et al. [11]: they measured the values 1134.2 and 135.0 eV for the $\text{Eu}_{3d5/2}$ and Eu_{4d} peaks, respectively. These values are not confirmed by our results. This could very well be attributed to problems in the energy calibration of their XPS spectra (see Section 1). The values published for $\text{Eu}_2(\text{C}_2\text{O}_4)_3$ and $\text{Eu}_2(\text{SO}_4)_3$, 1136.2 and 1137.7 eV, respectively [23] are neither consistent with ours. It can again be attributed to a calibration problem since the authors have used a thin gold layer on their samples for calibrating in BE their XPS spectra.

The core-level shifts here observed for europium are compared to those published for Group A metallic elements, and for transition metals mixed oxides [2,3,29–33]. These spectra published for several oxocompound $\text{M}_m\text{X}_x\text{O}_y$ showed higher core levels BE of M, when increasing the ionic character of M–O bonds: M is a more electropositive atom than X, consequently X–O bond are more covalent than M–O ones, substituting X for M in typically M–O–M units to form X–O–M would pull electrons away from M, thus making the M–O bond more ionic, and inducing an increase of core-levels BE of M in X–O–M as compared to X–O–M, i.e. in $\text{M}_m\text{X}_x\text{O}_y$, as compared to M_aO_b .

For $\text{M}=\text{Eu}$ (the most electropositive among the elements considered because located at their left in the Periodic Table) and that X corresponds to C (oxalate, acetylacetonate and carbonate), to N (nitrate) or S (sulfate), our results are in agreement with those obtained on Group A and transition metals oxides. As for O_{1s} BE value a correlation between the Pauling electronega-

Table 4

Shake-down satellite to parent photoelectron peak intensity ratios for $\text{Eu}_{3d5/2}$ and Eu_{4d} peaks

Nature of Eu(III) compound	Satellite/parent peak $\text{Eu}_{3d5/2}$ (in intensity)	Satellite/parent peak Eu_{4d} (in intensity)
Eu_2O_3	0.24	0.24
$\text{Eu}_2(\text{C}_2\text{O}_4)_3$	1.00	1.43
$\text{Eu}(\text{acac})_3$	0.23	0.29
$\text{Eu}_2(\text{CO}_3)_3$	0.27	0.19
$\text{Eu}_2(\text{SO}_4)_3$	0.16	0.13
$\text{Eu}(\text{NO}_3)_3$	0.13	0.11

tivity of the heteroatom X and the Eu_{3d} BE value was evidenced excepted for oxalate compound.

Finally, simultaneous using of the $\text{Eu}_{3d5/2}$ and Eu_{4d} core-level photoelectron peaks allows to discriminate different Eu(III) species. As for the O_{1s} photoelectron peak, from considerations based on electronegativity of heteroatom, it might very well be feasible to foresee BE values of other Eu(III) compounds sorbed on alumina surfaces.

3.3. Shake-down satellites of the Eu_{3d} and Eu_{4d} peaks

From Figs. 3 and 4, respectively, displaying $\text{Eu}_{3d5/2}$ and Eu_{4d} regions, it appears that the intensity of the shake-down satellite notably among the Eu(III) compounds. Shake-down satellite to parent photoelectron peak ratio were calculated for each Eu(III) compound for $\text{Eu}_{3d5/2}$ and Eu_{4d} regions and results are reported in Table 4. Evolution of these ratios is the same for $\text{Eu}_{3d5/2}$ and Eu_{4d} and XPS regions of Eu(III) oxalate are quite different from the other compounds of Eu(III). Indeed, these ratios are largely higher for Eu(III) oxalate (value of 1 against a maximum value of 0.27 for other compounds for $\text{Eu}_{3d5/2}$ and value of 1.43 against 0.29 for Eu_{4d}). Our results are in agreement with those reported in [23] on Eu(II) compounds that reveal a shake-down satellite to parent peak ratio for $\text{Eu}_{3d5/2}$ and Eu_{4d} much higher in the case of oxalate than for sulfate and oxide.

Moreover, the ratios are notably greater in the case of carbonate, oxalate, acetylacetonate and oxide than for nitrate or sulfate. However, our results can not be compared to those issued from literature since the only data about satellites exploitation for chemical environment determination are those of Laubschat et al. [12] in the case of Eu-transition metals compounds of EuM_5 type, which is very different from our Eu(III) oxocompounds.

The analysis of shake-down satellites of $\text{Eu}_{3d5/2}$ and Eu_{4d} , such as its intensity relatively to the parent photoelectron peak will allow to discriminate Eu(III) oxalate from the other compounds. Although oxide, carbonate, and acetylacetonate display a more intense satellite than for sulfate and nitrate, it is difficult to explain these trends because of a lack of information available in literature on shake-down satellites application to chemical environment determination.

4. Conclusion

To our knowledge, this study is the first XPS BE data base with a coherent binding energy calibration for Eu(III) com-

pounds differing by the chemical environment of Eu(III). The characteristics (signal shape, intensity, BE) of core-level photoelectron peaks O_{1s} , $Eu_{3d5/2}$ and Eu_{4d} , then of shake-down satellites of the last two peaks, have been reported and exploited. The results indicate that combining all these information is necessary to discriminate Eu(III) oxocompounds.

For each of the core-level peaks, all BE evolutions have been explained by ionicity/covalency changes of implied bonds from electronegativity differences of atoms and a good linear relation was evidenced for O_{1s} BE as a function of electronegativity. A satisfactory linear relation was equally evidenced for Eu_{3d} and Eu_{4d} BE. Our results are in perfect agreement with numerous data of literature concerning Group A and transition metals oxides and zeolites. Although our list of Eu(III) compounds is not exhaustive, a good comprehension of observed trends in BE evolution is sufficient to transpose these results to other Eu(III) species and to anticipate their BE values.

This binding energies data base would be applied to ternary systems $Al_2O_3/Eu(III)/$ organic complexing agent (for example, a carboxylic acid as oxalate issued from cellulose degradation) in order to identify chemical species of Eu(III) sorbed onto alumina surface.

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