# SATELLITES IN Ce 3d X-RAY PHOTOELECTRON SPECTROSCOPY OF CERIA

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Ce 3d X-ray photoelectron spectroscopy (XPS) spectra is characterized by the presence of "shake-up" and "shake-down" satellites, which complicate the analysis of the XPS data and especially the identification of different ionization states. The present paper proposes a new model for interpreting the 3d XPS lines of cerium oxide (CeO<sub>2</sub>). This model supposes 6 pairs of doublets with spin-orbit splitting, three corresponding of trivalent cerium and three corresponding of tetravalent cerium. The three components used for each ionization state correspond to the "shake-down" process, to the "parent" (Koopman) line, and to the "shake-up" line, in order of increasing binding energy. From the time dependence of Ce 3d and C 1s XPS spectra, a model for the contamination process is derived and also the length of the alkyl chains of the hydrocarbons may be estimated. The present analysis allowed a more accurate computation of the Ce 3d atomic sensitivity factor (ASF), in accord with the values found for other rare earths elements.

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## **1. Introduction**

Cerium oxides are important materials for applications in catalysis [1], photocatalysis, fuel cells, infrared filters or photoluminescence [2]. In particular, the cerium (III) oxide is commonly used as a catalyst for converting carbon monoxide in exhaust gases [3]. The additives introduced into the (diesel) fuel also contain cerium oxides. It follows immediately that the quantification of the quantity of cerium reduced is a crucial issue for all applications of cerium oxides.

The standard method to quantify the ionization states at surfaces is the X-ray photoelectron spectroscopy (XPS) [4]. This method is particularly suited for metals which may present more ionization states in their oxides [5].

In the case of cerium oxides, more particularly in the case of Ce 3d XPS spectra, the problem is complicated by the occurence of "shake-up" and "down-shake" satellites. A "shake-up" satellite appears as an additional line, at lower kinetic energy (or higher binding energy) than the original line (called in the following the "parent line", or "Koopman line"). This line corresponds to photoelectrons which lost a well-defined quantity of energy by excitation of a resonance in the sample [4]. The most frequent "shake-up" satellites are plasmon losses, where the photoelectron, before leaving the sample, loses the energy needed for excitation of a certain number of plasmons in the valence band of the sample. But there are also "shake-up" satellites, which correspond to additional, discrete, excitations. In atomic X-ray absorption spectra, these satellites are easily identified [6].

The "shake-down" satellites appear at lower binding energy (corresponding to higher kinetic energy) than the "parent" (Koopman) line, especially in atoms with 4f electrons, which could switch easily from a state specific to a localized orbital in one corresponding to a delocalized

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orbital. A "shake-down" satellite corresponds to the transfer of an additional kinetic energy of the outgoing photoelectron.

The "shake-down" process can be schematized as follows [7]:

(a) The incident photon is absorbed, the photoelectron is released leaving behind a core hole; its kinetic energy, in absence of any other additional processes, corresponds to the "parent line".

(b) In presence of the core hole, a valence state which can be localized (4f), initially unoccupied, becomes lower in energy than another valence state with lower angular momentum (6s, 5d), not localized, possibly hybridized with the 2p orbitals of oxygen (for example).

(c) One of these delocalized valence electrons is transferred on the localized state (4f), this is the proper "shake-down" process.

(d) Given that the state that has been just filled is localized, it shields more effectively the core hole (the attractive potential felt by the photoelectron on its way out to the analyzer decreases in absolute value) and therefore the kinetic energy of photoelectrons is higher.

The attribution of XPS lines in cerium oxide is a problematic issue for the community of photoelectron spectroscopy. The first article by Burroughs *et al.* [8] identified the "shake-down" line (indexed by *u* and *v*) and Koopman lines (or "parent") *u*", *v*" in the Ce 3d spectrum of CeO<sub>2</sub>, while the *u*', *v*' and *u*", *v*" states were related to the collective (multielectronic) excitations involving 5d, 6s and 6p electrons of Ce<sup>4+</sup>. (For the identification of these structures, the reader is invited to refer to Fig. 1.) A subsequent paper which examines the oxidation of cerium metal by XPS [9] proposed that the "parent" lines are *v*" and *u*", with *u*, *u*, *v*, *v*' corresponding to "shake-down" satellites, which involves charge transfer from O 2p orbital on Ce 4f or 5d; according to this work, *v*" and *u*" would correspond to "shake-up" satellites. However, this attribution, which is firmly stated in the paper cited earlier, was not retained in subsequent works [10-12]; the most authors have agreed that *v*" and *u*" represent the "parent" lines, while *v*", *u*" and *v*, *u* are "shake-down" satellites corresponding to the transfer of an electron from an O 2p orbital on a Ce 4f orbital, respectively the transfer of two O 2p electrons from valence band on two orbitals localized on Ce 4f.

There are several objections that can be formulated:

(i) Firstly, as explained in Ref. [9], this attribution would imply a very high chemical shift between the "parent" lines of  $Ce^{3+}$  and  $Ce^{4+}$ , approximately 12.3 eV. At the same time, when the ionization state changes only by one unit, the chemical shifts is on the order of a few (1-2) eV, as shown as for the transition metals (vanadium, from  $V^0$  to  $V^{5+}$  [5]) or very recently, for the rare earth elements (samarium, from  $Sm^0$  to  $Sm^{3+}$  [13,14]). In the case of V 2p, it has been shown in Ref. [5] that the total displacement from  $V^0$  to  $V^{5+}$  is of about 5.5 eV, with an energy difference of 1 eV between the neighboring higher ionization states. In the case of Sm 3d, the energy difference between Sm<sup>0</sup> and Sm<sup>3+</sup> is approximately 9 eV, but between Sm<sup>2+</sup> and Sm<sup>3+</sup> it is only approximately 2 eV [13].

(ii) Secondly, the doublet (u, v), which represent the most intense lines, is assigned, according to the last hypothesis, to a 4f<sup>2</sup> configuration, i.e. to multiple excitations involving three electrons: primary photoelectrons and two electrons transferred to 4f<sup>2</sup> states.

Both these objections have led us to reconsider the attribution of the Ce 3d photoelectron by getting inspired also by the Ce<sup>3+</sup> spectrum provided by Ref. [10], by using the analysis of cerium reduction in a hydrogen atmosphere, according to Ref. [12] and also the analysis of the cerium reduction by X-ray radiation, from Ref. [15]. Thus, at present we can say that the peak ( $\nu'$ , u') correspond to the "parent" lines of Ce<sup>3+</sup>, with 4f<sup>4</sup> configuration.

A "shake-down" satellite of the 4f<sup>2</sup> state of Ce<sup>3+</sup> is somehow mixed with lines (v, u) and denoted by ( $v_0$ ,  $u_0$ ) in Ref. [3, 12]. Moreover, Ce<sup>3+</sup> does not show a "shake-down" satellite with the participation of three electrons. Instead, a "shake-up" satellite of Ce<sup>3+</sup> is visible (though quite difficult) at an energy of approximately 895 eV in Fig. 6 of Ref. [10] and in Fig. 10 of Ref. [12]. Consequently, the strategy to be followed is to not neglect the "shake-up" processes neither for Ce<sup>3+</sup>, nor for Ce<sup>4+</sup>. On the other hand, it seems reasonable to restrict the analysis, at least in terms of "shake-down" processes, to the collective processes involving no more than two electrons. It follows therefore that the experimental spectrum should be simulated with 6 pairs of lines ("parent", "shake-up" and "shake-down", both Ce<sup>3+</sup> and Ce<sup>4+</sup> ionization states), separated by spin-

orbit splitting (in total 12 lines), which was not done in any work so far, except for the simulation initiated by our group in Ref. [2], but where the experimental data statistics and the fact that it did work with monochromatic radiation made it difficult the procedure of curve fitting.

At the same time, this paper will attempt to correlate the signals obtained for Ce 3d with other photoemission lines observed, C 1s and O 1s. First, this will aim to test the composition obtained from XPS analysis, possibly the derivation of the atomic sensitivity factor of Ce 3d, as the standard Reference [16] does not give an accurate value for this sensitivity factor (a value of 10 is specified in parentheses). Also, a possible origin of reduced cerium Ce<sup>3+</sup> will be derived from this kind of analysis: an hypothesis will be formulated that Ce<sup>3+</sup> is formed during the interaction with CO molecules from the residual gas during the XPS analysis, a process yielding to the synthesis of carboxylic acids on the grains surface.

## 2. Experimental

The CeO<sub>2</sub> powder (Sigma-Aldrich, 99.995 % purity) was pressed onto carbon tapes, by using tools cleaned by ultrasons in pure isopropanol, and placed in the photoelectron spectroscopy equipment. Al K<sub>a1</sub> monochromatic radiation was used (hv = 1486.74 eV), and the electron analyzer operated with a pass energy of 20 eV. In these conditions, the combined experimental broadening (analyzer + width of excitation line) is approximately 0.5 eV [17]. However, after deconvolutions, the result is a gaussian width of the lines in the order of 3.5 to 4 eV for Ce 3d, 2.6 to 3.1 eV for C 1s and 2.4 eV for O 1s. These widths substantially higher than expected values for these experimental conditions are evidence of the surface disorder of ceria crystallites. To compensate for surface charging effects an electron flood gun was used, with 1 eV electron kinetic energy from 1 eV and 100  $\mu$ A electrons current. The X-ray gun power was maintained at 400 W, with acceleration voltage of 12 kV. During the measurement, the pressure in the analysis chamber was in the range of 10<sup>-10</sup> mbar. We did not operate any binding energy corrections of the experimental spectra: all discussions that follow refer to the value of the binding energies measured.

Continuous measurements cycles (Ce 3d + C 1s) were performed. A measurement cycle lasted 10 hours, of which 9 hours are needed for Ce 3d and 1 hour for C 1s. These measurements were carried out in order to increase the statistics and, at the same time, to monitor any changes in the composition and/or the binding energies during the measurement. As discussed below, this approach allowed the identification of the reactions at the surface as a result of the interaction with residual gas molecules, when the samples are subjected to the measurement (X-ray and flood gun electron fluxes). Also, at the end of measurements, the O 1s spectrum was recorded.

XPS spectra were 'deconvoluted' by using combinations of Voigt profiles with their integrals [18, 19]; these integrals take into account the effects of energy loss by inelastic collisions of photoelectrons leaving the sample. It has been demonstrated several years ago that associating to each peak its separate inelastic background allows deriving if the atoms responsible for this peak are placed on the surface of the sample or in its bulk [18,20].

## 3. Results and discussions

## 3.1. Presentation of results

Figure 1 shows Ce 3d spectra obtained at intervals of 10 hours, as presented in the previous paragraph. It is observed that the signal intensity of Ce 3d decreases in time. Also, there is a shift of spectra in time towards lower binding energies.

Figure 2 shows the C 1s spectra obtained in the same conditions, namely each spectrum is separated by 10 hours to the previous one. In this case, it is seen that the C 1s signal increases with time. Therefore, we have a first explanation of intensity variation in time for Ce 3d: the sample is contaminated with carbon and since the inelastic mean free path of photoelectrons from 3d levels of cerium is rather low,  $\lambda_{Ce} \approx 7$  Å [4], the cerium signal decreases in time, and at the same time the C 1s signal increases.

The main purpose of this study was to analyze the photoelectron spectra of Ce 3d. As discussed in the Introduction, the analysis had to be carried out with 6 pairs of Voigt profiles and associated integrals  $I = \int V dx$  [18], which were attributed to the two states Ce<sup>3+</sup> and Ce<sup>4+</sup>, each state showing three pairs of Voigt profiles [19] (owing to the spin-orbit splitting  $3d_{5/2}$  -  $3d_{3/2}$ ); thus, each ionization state presents the characteristic lines of the original state ("parent line") plus "shake-up" and "shake-down" satellites.



Fig. 1. XPS spectra of Ce 3d measured consecutively at intervals of 10 hours.

The formula used for the simulation was:

$$F(\mathbf{p}, x) = \sum_{j=1}^{3} A_{j} \begin{cases} \frac{br}{br+1} \Big[ V(W_{L}^{(1)}, W_{G}, x - E_{j}) + b_{j} I(W_{L}^{(1)}, W_{G}, x - E_{j}) \Big] \\ + \frac{1}{br+1} \Big[ V(W_{L}^{(2)}, W_{G}, x - E_{j} - \Delta E^{(3+)}) + b_{j} I(W_{L}^{(2)}, W_{G}, x - E_{j} - \Delta E^{(3+)}) \Big] \end{cases}$$
(1)  
+ 
$$\sum_{j=4}^{6} A_{j} \begin{cases} \frac{br}{br+1} \Big[ V(W_{L}^{(1)}, W_{G}, x - E_{j}) + b_{j} I(W_{L}^{(1)}, W_{G}, x - E_{j}) \Big] \\ + \frac{1}{br+1} \Big[ V(W_{L}^{(2)}, W_{G}, x - E_{j} - \Delta E^{(4+)}) + b_{j} I(W_{L}^{(2)}, W_{G}, x - E_{j} - \Delta E^{(4+)}) \Big] \end{cases} + \alpha x + \beta$$

where p is the vector of fitting parameters, formed by three widths, Gauss for instrumental broadening  $W_G$ , Lorentz  $W_L^{(1)}$  and  $W_L^{(2)}$  for the inherent widths of spectral lines (they were considered different to take into account the additional Coster-Kronig channels for the state with lower angular momentum J [20]), spin-orbit splitting  $\Delta E^{(3+)}$  and  $\Delta E^{(4+)}$ , which are different for different ionization states, as recently demonstrated in Ref. [13], the branching ratio br (it was fixed at its theoretical value of 1.5 for d orbitals), then, for each component: the energy, the integral amplitude and the coefficient of inelastic background, or  $E_i$ ,  $A_i$  and  $B_i$ , j ranging between 1

and 6. The first three terms of (1) correspond to  $Ce^{3+}$  states; the last three terms correspond to  $Ce^{4+}$  states. Finally, a base line  $\alpha$  and a slight slope of spectrum  $\beta$  are added. Consequently, the fitting was performed with 25 parameters. 23 of these are tabulated in the Appendix.



Fig. 2. XPS spectrum of C 1s measured at intervals of 10 hours. For clarity, an offset of 50 cps on ordinate axis between each two successive spectra was introduced.

The result is shown in Figures 3 (a-h). One may remark the satisfactory quality of the fit, with the exception of the large binding energies area, where additional structures appear (plasmonic losses), which were not considered in the simulation.

Also, in Figures 4 (a-h) are represented XPS spectra of C 1s deconvoluted by using a combination of the three Voigt singlets and associated inelastic backgrounds. It is observed that, with the exception of the last spectrum corresponding to the most contamined sample, two lines were sufficient to simulate the experimental spectra, one exhibiting an important inelastic background and the other with almost zero inelastic background. Therefore, in view of considerations of Ref. [18], we consider that the main line of the C 1s corresponds to contaminants present on the sample surface, and the line of higher binding energy originates from the bulk. The fitting parameters for C 1s are also tabulated in Appendix.



Fig. 3. XPS spectra of Ce 3d represented in Fig. 1, together with simulations (deconvolutions) by using the formula (1).



*Fig. 4. XPS spectra of C 1s in Fig. 2 together with simulations (deconvolutions) by using a combination of three Voigt lines and associated inelastic backgrounds.* 

Figure 5 represents the O 1s spectrum, recorded at the end of the measurement series with a simulation using four Voigt singlets (with only two or three components, the result was not satisfactory). The assignment of all these components will be discussed in a later paragraph. The Appendix presents the parameters of this deconvolution.



Fig. 5. XPS spectrum of O 1s, together with a simulation by using four Voigt profiles and associated inelastic backgrounds.

## 3.2. Binding energies

In Figure 6, we represented the binding energies obtained for all components of the previous analysis, for Ce  $3d_{5/2}$  and C 1s, and the correlation between the energies of cerium components and that of the major component for C 1s. In Fig. 6 (a), the different colors were used to illustrate the states that were assigned to Ce<sup>3+</sup> (red) and Ce<sup>4+</sup> (blue). As can be observed in Fig. 3, the main line ("parent line") has a relatively low intensity, as compared to "shake-up" and "shake-down" satellites, especially for Ce<sup>4+</sup>. Basically, the most prominent lines of the whole manifold of Ce 3d are the "shake-up" and "shake-down" satellites of Ce<sup>4+</sup>. Results of integrated intensity for each doublet are shown in Figure 7.



Fig. 6. (a) Binding energies obtained for Ce  $3d_{5/2}$  of all the analyses shown in Fig. 3; (b) Similarly, the C 1s energy components obtained from the analysis shown in Fig. 4 (c) Dependences of Ce  $3d_{5/2}$  binding energies on the binding energy of C 1s dominant component.



Fig. 7. Dependence of integrated amplitude from the Ce 3d spectrum fitting on the spectrum number (time spent during the measurements).

Concering the C 1s spectrum, the evolution of the integrated intensity shows an constant increase in time of the intensity of the main line (binding energy of ~ 289.5 to 288.5 eV), indicating the progress of a surface reaction. The value of this energy indicates a positive ionization state of the carbon, approximately equal to that of the carbonate ion  $CO_3^{2-}$  [21]. In other words, it is possible that, subsequent to the surface reaction, cerium carbonate is formed on the surface, possibly according to a reaction such as:  $2 CeO_2 + CO + CO_2 \rightarrow 2 Ce_2(CO_3)_3$ , where carbon monoxide and carbon dioxide originate from residual gas of the ultrahigh vacuum chamber. Examples of residual gas analysis from this chamber, revealing the presence of CO and CO<sub>2</sub> are shown in Refs. [22,23]. X-ray excitation and electron beam influence of flood gun increase the probability of occurrence of reaction centres on the surface, leading to the sample contamination [9, 22]. Also, the O 1s spectrum presents a dominant line for a binding energy of 531.77 eV, corresponding to the formation of the radical COO<sup>-</sup> or CO<sub>3</sub><sup>2-</sup> [21, 24].

An interesting aspect that was revealed by these experiments is the constant shift of both lines of Ce 3d and of C 1s towards lower binding energies, by approximately 1 eV for C 1s and approximately 1.5 eV for Ce 3d, as the sample it contaminated. This effect can be attributed to the band bending at the CeO<sub>2</sub> surface, as it becomes contaminated [25-28]. Assuming, for simplicity, that the contamination layer is conductive, the observed band bending implies that the CeO<sub>2</sub> workfunction is about 1-1.5 eV lower than that of the contamination layer [25,26]. In other words, the Fermi level in CeO<sub>2</sub> is quite close to the minimum of the conduction band, whereas, normally, the workfunction of CeO<sub>2</sub> is about 4.7 eV [29]. This would mean that ceria is n doped, at least nearly the surface, which is possible if we consider the possibility of oxygen vacancies formation.

#### 3.3. Intensity analysis

It should be noted from the beginning that trying to interpret the evolution of  $Ce^{3+}$  and  $Ce^{4+}$  intensities and as well of the C 1s intensity by supposing the formation at the surface of cerium carbonate only was unsuccessful. The carbon intensity of the contamination layer is too high. In the following, we will present a simplified model, according to which the bulk is composed by  $CeO_2$ , containing  $Ce^{4+}$  and  $Ce^{3+}$ , and on the surface a compound such as  $Ce(ROO)_3$  is formed, where R is an alkyl radical, and the cerium presents only a ionization state corresponding to  $Ce^{3+}$ .

The proportion of  $Ce^{3^+}$  in  $CeO_2$  will be noted by *p*. The thickness of the contaminantion layer, assumed uniform, is *d* and  $\lambda_{Ce}$  respectively  $\lambda_C$  are, respectively, inelastic free paths of photoelectrons originating from Ce 3d and C 1s ( $\lambda_{Ce} < \lambda_C$ ).

Let's note by  $\alpha$  the atomic concentration of Ce<sup>4+</sup> in CeO<sub>2</sub> (normally  $\alpha = 1/3$ ),  $\beta$  the atomic concentration of Ce<sup>3+</sup> in the contamination layer, and  $\gamma$  the atomic concentration of carbon in the layer.

Let's note by  $I_0$  the integrated intensity of the C 1s photoemission, then in the case of a 1:1 ratio between Ce and C, the integrated intensity of the Ce 3d photoemission would be  $rI_0$ , where r is the ratio between the atomic sensitivity factors (ASF) of Ce 3d and C 1s. According to Ref. [16], r = ASF (Ce 3d) / ASF (C 1s)  $\approx 10 / 0.25 = 40$ .

By considering the effects of the inelastic mean free part, one can write the integrated intensity (for Ce 3d we will consider the integrated intensity of the spin-orbit split doublet).

$$I(\operatorname{Ce}^{4+}) = \alpha r I_0 \exp\left(-\frac{d}{\lambda_{\operatorname{Ce}}}\right)$$
(2.1)

$$I(\operatorname{Ce}^{3+}) = \beta r I_0 \left\{ 1 - \exp\left(-\frac{d}{\lambda_{\operatorname{Ce}}}\right) \right\} + p \alpha r I_0 \exp\left(-\frac{d}{\lambda_{\operatorname{Ce}}}\right)$$
(2.2)

$$I(C) = \gamma I_0 \left\{ 1 - \exp\left(-\frac{d}{\lambda_{Ce}}\right) \right\}$$
(2.3)

Hence, two dependencies may be tested experimentally:

$$I(\operatorname{Ce}^{4+}) = \frac{\alpha}{\alpha p - \beta} I(\operatorname{Ce}^{3+}) - \frac{\alpha \beta r I_0}{\alpha p - \beta}$$
(3.1)

$$I(\operatorname{Ce}^{4+}) = \alpha r I_0 \left\{ 1 - \frac{I(\operatorname{C})}{\gamma I_0} \right\}^{\lambda_{\operatorname{C}} + \lambda_{\operatorname{Ce}}}$$
(3.2)

The total intensities of  $Ce^{3+}$  and  $Ce^{4+}$  were considered as the sum of the doublets areas "parent" + "shake-up" + "shake -down". (If the results are coherent, this means also that the allocation of lines by the simulation of Ce 3d spectrum is correct.) For C 1s, only the line binding energy of approximately 289 eV is considered.

In Figure 8 we represented the two dependencies, together with the fit using the formulas (3.1) and (3.2).

Fitting the points from Fig. 8 (a) with formula (3.1) yielded  $\alpha/(p\alpha-\beta) \approx 3.95$  and  $\alpha\beta rI_0 / (p\alpha-\beta) \approx 17000$ . It follows  $\beta rI_0 \approx 4300$ .

Fitting the points from Fig. 8 (b) with formula (3.2) resulted  $\lambda_C / \lambda_{Ce} \approx 2$ ,  $\alpha r I_0 \approx 40000$  and  $\gamma I_0 \approx 3700$ . It follows  $\alpha/\beta \approx 9.3$  and  $\alpha r/\gamma \approx 10.8$ . If we suppose that  $\alpha = 1/3$ , this means that  $\beta \approx 1/28$ , that we can already say that the R radical contains 7 atoms, so that all proposed compound Ce(ROO)<sub>3</sub> containing 28 atoms. We shall not take into account the hydrogen atoms (as it is usual in organic chemistry), then R is an alkyl chain containing 7 carbon atoms. Under these conditions, we can derive  $\gamma = 7 \times 3/28 = 0.75$  and, by introducing the value of  $\alpha$ , it results  $r = 24.45 \pm 0.09$ . In other words, the atomic sensitivity factors of Ce 3d should be approx. 6.1. This value is close to that was derived by a similar analysis for Sm 3d, ASF(Sm 3d)  $\approx 6.36$  in Ref. [13].

Also, it is normal that the ASF for Ce 3d is lower than that for Sm, since it is known that the atomic sensitivity factors increase when the binding energies approach the excitation energy, and the binding energy of Sm 3d is higher than Ce 3d.

The last value that can be determined from this analysis is the proportion of trivalent cerium in CeO<sub>2</sub> volume,  $p \approx 1/3.95 + 3/28 \approx 0.36$ . At this point, we consider also the amplitudes obtained for O 1s. We will consider only the final spectra of Ce 3d and O 1s. By normalizing to the previously derived ASF (Ce 3d), it yields that the intensity of Ce<sup>4+</sup> is close 562 eV x cps.

For O 1s, we consider the components with the binding energies of 529.86 eV, 534.42 eV and 526.91 eV. The total intensity, normalized to ASF (O)  $\approx 0.66$ , yields 1037 eV x cps. This leads to a stoichiometry [O]/[Ce]  $\approx 1.85$ . Thus, we observe oxygen vacancies at the CeO<sub>2</sub> surface,

1544

which, on one hand, explains the band bending at the interface as soon as the sample is contamined and, on the other hand, explains the presence of  $Ce^{3+}$  in the sample.



Fig. 8. (a) Dependence of the integral intensity of tetravalent cerium on that of trivalent cerium, together with a linear fitting (3.1); (b) Integral intensity of tetravalent cerium vs the integral intensity of C 1s, together with a nonlinear fitting formula (3.2).

Also, the ratio of carbon and oxygen in the contamination layer can be estimated. The main component of C 1s for the last spectrum recorded is about 1780 eV x cps. By normalizing to ASF(C)  $\approx 0.25$ , one obtains an intensity of approx. 7200 eV x cps. The O 1s component at 531.77 eV has an intensity of approximately 1970 eV x cps, and by normalizing it becomes approximately 2990 eV x cps. Hence, the ratio between carbon and oxygen in the contamination layer is around 2.4. Or, if one considers the alkyl radical containing 7 carbon atoms and 2 oxygen atoms, the ratio should be 3.5. It follows that in the O 1s component which has been taken into account for this latter calculation, there is some oxygen in a similar chemical state, but unbound in compounds formed by cerium at the interface. In fact, it is quite possible that a very thin layer which contains oxygen on the surface (for example, physisorbed water) might induce a considerable change in the ratio observed between carbon and oxygen in the contamination layer. For example, if the ceriumcontaining contamination layer we have discussed so far is covered with a second layer containing only oxygen (and hydrogen, if necessary) with the thickness  $d_1$ , the intensity of carbon in the layer of contamination becomes  $I_{\rm C}^{(0)} \exp(-d_1/\lambda)$ , that of oxygen in the layer of contamination will follow the same dependence,  $I_{\rm O}^{(0)} \exp(-d_1/\lambda)$ ; to this intensity one has to add the intensity of the oxygen in the additional layer  $I_0^{(1)}$  {1 - exp(-  $d_1/\lambda$ )}. The ratio between carbon and oxygen will be in this case (we assume that the inelastic mean free path is the same for C 1s and O 1s,  $\lambda$ ):

$$\frac{I_{\rm C}}{I_{\rm O}} = \frac{I_{\rm C}^{(0)}}{I_{\rm O}^{(0)} + I_{\rm O}^{(1)} \{\exp(d_1/\lambda) - 1\}} = \frac{I_{\rm C}^{(0)}}{I_{\rm O}^{(0)}} \times \frac{1}{1 + (I_{\rm O}^{(1)}/I_{\rm O}^{(0)})} \exp(d_1/\lambda) - 1\}$$
(4)

It is easily seen that when  $I_0^{(1)}/I_0^{(0)} \approx 2$  (assuming that the surface is saturated with molecules containing oxygen and not carbon) and  $I_C^{(0)}/I_0^{(0)} \approx 3.5$ , we obtain  $I_C^{(0)}/I_0^{(0)} \approx 2.4$  if  $d_1 \approx 0.2 \lambda \approx 2$  Å, namely  $d_1$  corresponds roughly to a monoatomic layer. The existence of this additional oxygen at the surface affects somehow the previous considerations regarding the C, Ce<sup>3+</sup> and Ce<sup>4+</sup> intensities, since these intensities will be attenuated, and not by the same factor. The attenuation will be more pronounced for cerium intensities than for carbon ones, and these factors will be  $\exp(-2/7) \approx 0.75$  for cerium and  $\exp(-2/14) \approx 0.86$  for carbon. This can be introduced into above considerations by changing the *r* parameter (ASF ratio between Ce 3d and C 1s) by a factor of 1.15. On the other hand, by taking into account the stoichiometry (ratio of oxygen/cerium) other than 2 (CeO<sub>1,85</sub>), the parameter  $\alpha$  is reduced by approximately 5 % and this will reduce the ASF derived for Ce 3d. Taking into account both aspects, we obtain an ASF value (Ce) of about 6.6, which returns to a stoichiometry of 2.00. However, we tend to consider a stoichiometry slightly lower than 2, which justifies the observed band bendings, with n-type doping of the sample surface. Note also that a lower stoichiometry in oxygen will induce higher values of the parameter  $\alpha$  and thus also of the parameter  $\beta$  from this analysis. For example, if instead of 3,  $\alpha^{-1} = 2,85$ , that  $\beta^{-1} \approx 26,5$  which is about the average of 28 and 25, therefore approximately one half of the carboxylic radicals will contain 6 carbon atoms and two oxygens, and the remaining radicals contain 7 carbon atoms and two oxygens. It is straightforward that all of the considerations presented are valid only in average. It is possible that some of the carboxylic acid radicals may contain even more carbon, and others may be of smaller size, up to the presence of the COO<sup>-</sup> or CO<sub>3</sub><sup>2-</sup> radicals.



Fig. 9. Model of contamination of CeO<sub>2</sub> surfaces, by taking into account all measurements by photoelectron spectroscopy (Ce 3d, C 1s, O 1s).

One can sketch a model of the contamination of the  $CeO_2$  surface (Figure 9). At the surface, a compound is formed containing the carboxylic radicals bounded to trivalent cerium, and, on the surface of this compound, excess oxygen is identified, most likely a monoatomic layer of water or of physisorbed oxygen molecules.

This result raises some questions about the catalytic properties of reduction of the carbon monoxide presented by CeO<sub>2</sub>. We recall also that we have detected the formation of a relatively high Schottky barrier (at least 1 eV) at the surface when the sample is contaminated. We recall that, due to oxygen vacancies that we have identified, the areas of the surface present n-type doping. This means that there is a migration of electrons from CeO<sub>2</sub> to the contaminant, to equalize the Fermi levels [25,26,28]. If the contaminant molecules are not connected to the ground, this means that these areas will become negatively charged and chemically active for the catalytic reduction processes. In this outline, the catalytic compound is, in fact, the cerium carboxide from the surface. The cerium oxide do not intervene directly in the catalytic process, except by the fact that it produces the required active charge at the surface, owing to its low workfunction, and eventually provides cerium (eventually, also oxygen) for the formation of the interface compound.

## 4. Conclusions

A new model was proposed to interpret the Ce 3d lines from photoelectron spectra of CeO<sub>2</sub>. The proposed model uses 6 pairs of doublets with spin-orbit splitting, three corresponding of trivalent cerium and three corresponding of tetravalent cerium. Each ionization state is manifested by three components, one corresponding to Koopman's line, or "parent" and two to "shake-up" and "shake-down" satellites. The differences of energy are about 10 to 10.5 eV between the "shake -up" line and the parent line (SU - P), and from 4.9 to 5.4 eV between "parent" line and the "shake -down" line (P - SD) for Ce<sup>4+</sup>; for Ce<sup>3+</sup>, the differences are about 3.9 eV (SU - P) and approx. 4.7 to 5.1 eV (P - SD). The total intensity of each state of ionization of use for compositional analysis is the sum of three components. Also, the chemical shift between the "parent" lines of Ce<sup>3+</sup> and Ce<sup>4+</sup> is absolutely reasonable in this case, it varies between 2.3 eV for the sample immediately after introduction (first spectrum Ce3d) and 2 eV after 80 hours of measurements.

1546

The CeO<sub>2</sub> sample is contaminated during the XPS measurement, and synthesize a compound of approximate formula  $Ce^{3+}(ROO)^{-}_{3}$ , where R is an alkyl radical containing approximately 6-7 carbon atoms. On the surface of the contamination layer, it seems that monolayer mainly composed of oxygen (O<sub>2</sub> or H<sub>2</sub>O) is adsorbed. All intensity analyses are coherent between the Ce 3d, C 1s and O 1s spectra. Also, these analyses allowed the deduction of more accurate values of atomic sensitivity factor (ASF) of Ce 3d (between 6.1 and 6.6), a value in agreement with the current experience on other rare earths.

It was also proven that the volume of  $\text{CeO}_{2-\delta}$  is slightly sub-stoichiometric ( $\delta \approx 0.15$ ), the oxygen vacancies induce an n-type doping which, in the presence of contaminants of conductive properties owing to the excess of carbon, induces a band bending in ceria to higher energy values (in absolute value), specific for the contact between a semiconductor and a metal with higher workfunction [25,26].

The current analysis is, in our opinion, a significant advance in terms of quantitative analysis of spectra containing cerium or compounds based on ceria, widely used in modern technology, and where specifically the surface properties and the oxidation-reduction state are the most important properties to be determined, for all practical applications.

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1548

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## Appendix

Spectra	Ce 3d	Ce 3d	Ce 3d	Ce 3d	Ce 3d	Ce 3d	Ce 3d	Ce 3d
Parameter	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$W_L^{(1)}$ (eV)	0.245	0.239	0.238	0.236 0.234		0.234	0.233	0.233
$W_L^{(2)}$ (eV)	0.206	0.193	0.190	0.188	0.186	0.186	0.186	0.186
$W_G(eV)$	4.041	3.744	3.633	3.564	3.511 3.497		3.482	3.468
$\Delta E^{(1)} (eV)$	18.38	18.31	18.30	18.29	18.29	18.307	18.32	18.33
$\Delta E^{(2)} (eV)$	23.16	22.91	22.86	22.78	22.73	22.81	22.85	22.95
br	1.5	1.5	1.5	1.5 1.5		1.5	1.5	1.5
$E_1$ (eV)	880.90	880.47	880.23	880.10 880.01		879.95	879.88	879.80
$A_1$ (eV·cps)	7658	7645	7159	6508	5971	5622	5064	4645
$b_1$	0.061	0.059	0.054	0.049	0.045	0.042	0.039	0.037
$E_2 (eV)$	886.02	885.46	885.14	884.92	884.77	884.71	884.58	884.52
$A_2$ (eV·cps)	9230	7866.	7497	6921	6677	6350	5970	5639
$b_2$	0.000	0.007	0.010	0.010	0.011	0.011 0.011		0.012
$E_3$ (eV)	889.94	889.36	889.10	888.82	888.67	888.60	888.47	888.40
$A_3$ (eV·cps)	4743	3539	3471	3334	3265	3139	3016	2851
$b_3$	0.322	0.307	0.296	0.298	0.301	0.307	0.315	0.323
$E_4 (eV)$	882.93	882.41	882.16	881.99	881.88	881.82	881.74	881.68
$A_4$ (eV·cps)	23399	18891	16577	14460	13165	12241	11353	10385
$b_4$	0.056	0.047	0.039	0.033	0.029	0.025	0.020	0.015
$E_5 (eV)$	888.36	887.62	887.25	887.00	886.84	886.76	886.62	886.57
$A_5$ (eV·cps)	8887	7309	6484	5689	5189	4863	4546	4184
$b_5$	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$E_6$ (eV)	898.47	897.89	897.63	897.45	897.34	897.26	897.18	897.09
$A_6$	23532	18934	16390	14152	12727	11661	10571	9476
$b_6$ (eV·cps)	0.063	0.074	0.085	0.094	0.101	0.108	0.114	0.124

Table 1. Parameters for deconvolution of C 3d.

Spectra	C 1s	O 1s							
Parameter	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(8)
$W_L(eV)$	1.089	0.383	0.344	0.331	0.348	0.352	0.255	0.283	0.214
$W_G(\mathrm{eV})$	2.602	2.845	2.802	3.148	3.137	3.097	3.117	3.199	2.438
$E_1$ (eV)	293.93	283.60	283.83	283.80	283.80	283.81	283.81	283.72	529.86
$A_1$	0.000	15.5	1.6	0.603	0.046	0.1	0.032	45.5	611.6
(eV·cps)									
$b_1$	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.000	0.080
$E_2$ (eV)	289.45	289.30	289.33	289.32	289.15	288.96	288.67	288.49	531.77
$A_2$	642.3	781.03	1050.8	1399.2	1475.4	1573.2	2144.7	2266.4	2744.0
(eV·cps)									
$b_2$	0.000	0.062	0.035	0.000	0.000	0.000	0.000	0.000	0.000
$E_3$ (eV)	293.57	294.41	294.59	293.98	293.91	293.78	293.51	293.56	534.42
$A_3$	163.7	86.7	104.5	165.6	140.6	121.3	164.9	191.56	218.7
(eV·cps)									
$b_3$	0.294	0.000	0.048	0.306	0.301	0.323	0.277	0.249	0.105
$E_4 (eV)$									526.91
$A_4$									122.2
(eV·cps)									
$b_4$									0.071

Table 2. Parameters for deconvolution of C 1s and O 1s.