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Submitted on 1 Jan 1990

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Core-level photo-emission and -absorption spectra in Rare Earth hydroxide series

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(Reçu le 24 octobre 1989, accepté le 19 décembre 1989)

Résumé. — Nous calculons les spectres de photoémission 3d des composés R(OH)₃ avec R = La, Ce, Pr, Nd et Sm et ce, en utilisant le modèle d'Anderson à une impureté. Ensuite par l'analyse des résultats expérimentaux correspondants, nous pouvons estimer la valeur des paramètres fondamentaux de notre modèle pour la série envisagée des hydroxydes. De même, nous interprétons les spectres d'absorption 2p de La(OH)₃, Ce(OH)₃ et Sm(OH)₃ qui ont été observés récemment : pour ce faire, en plus des paramètres précédemment introduits, nous avons besoin de deux nouveaux paramètres (Ufd et Udc) qui sont spécifiques aux processus d’absorption. A partir de notre étude systématique de la série des hydroxydes de lanthanides (du moins de La à Sm) nous avons déduit que le spectre de photoémission obtenu expérimentalement dans Ce(OH)₃ n’est probablement pas celui d’un échantillon authentique — à cause de la contamination de surface. Au contraire, nous pouvons prédire la forme théorique d’un spectre de photoémission 3d intrinsèque à Ce(OH)₃ et en plus nous présentons quelques résultats expérimentaux préliminaires (mais nouveaux) sur ce composé.

Abstract. — We calculate the 3d-photoemission spectra of R(OH)₃ compounds (with R = La, Ce, Pr, Nd and Sm) by using the single impurity Anderson model. Then by analysing the corresponding experimental data we are able to estimate the key parameter values of the hydroxides considered within our model calculation. We also analyse the 2p-photoabsorption spectra of La(OH)₃, Ce(OH)₃ and Sm(OH)₃ which have been observed recently : in addition to the parameters already introduced we need two new parameters (Ufd and Udc) which are specific to the photoabsorption process. From our systematic study of the lanthanide hydroxide series (at least from La to Sm) we deduce that the available experimental 3d-photoemission spectrum of Ce(OH)₃ is probably not consistent with a genuine sample of Ce(OH)₃ — due to surface contamination. Nevertheless we are able to predict the corresponding intrinsic 3d-photoemission spectrum and in addition we present some new preliminary experimental measurements on that compound.
1. Introduction.

In this paper we are interested in the core-level spectroscopy of Rare Earth hydroxides: (i) a first class of these compounds would correspond to formally « tetravalent » hydroxides i.e. \( \text{R(OH)}_4 \) where \( \text{R} \) is a Rare Earth element. Unfortunately these tetrahydroxides do not seem to form well defined crystals: for example a sample of nominal composition \( \text{Ce(OH)}_4 \) has been obtained in an amorphous state; its 3d-XPS (photoemission) spectrum (see [1] and Refs. therein) is then very similar to that of \( \text{CeO}_2 \) crystals, i.e. essentially a three peak structure (see [2, 3] and Refs. therein); also, the essential feature of the 2p-XAS (absorption) spectrum for the considered \( \text{Ce(OH)}_4 \) sample is the occurrence of a two-peak structure like in \( \text{CeO}_2 \) compounds [1, 3-4]; (ii) another class of more common Rare Earth hydroxides is given by « trivalent » crystals, i.e. \( \text{R(OH)}_3 \). In the present paper we only focus on this second class of compounds which are interesting for example in connection with their possible role in catalysis; in particular, we develop a systematic theoretical analysis of the experimental data on 3d-XPS and 2p-XAS spectra in \( \text{R(OH)}_3 \) with \( \text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd} \) and \( \text{Sm} \).

As regards the 3d-XPS spectra for the series of \( \text{R(OH)}_3 \), the most extensive measurements have been carried out several years ago by Tatsumi et al. [5], essentially showing — except for \( \text{Sm(OH)}_3 \) — a two-peak structure: for example (i) the spectrum of \( \text{La(OH)}_3 \) resembles that obtained for \( \text{LaO}_3 \) [6] whereas (ii) the spectrum of \( \text{Ce(OH)}_3 \) also exhibits two peaks, as in \( \text{CeO}_3 \) [3, 7] but the energy spacings between the peak positions are quite different from one result (oxide) to the other (hydroxide). We will discuss the data on \( \text{Ce(OH)}_3 \) later in this paper. More recently Beaurepaire et al. [1] measured the 2p-XAS of \( \text{R(OH)}_3 \) trihydroxides with \( \text{R} = \text{La}, \text{Ce} \) and \( \text{Sm} \): they found one peak at the absorption threshold due to the dipole allowed transition \( 2p \rightarrow 5d \), i.e. the usual « white line » in the \( \text{L}_3 \) edge spectrum.

The theoretical analysis of 3d-XPS within the framework of the filled band single impurity Anderson model has been first proposed for \( \text{CeO}_2 \), \( \text{Ce}_2\text{O}_3 \) and \( \text{La}_2\text{O}_3 \) [2, 3, 6] and then carried out for \( \text{RO}_2 \) and \( \text{R}_2\text{O}_3 \) [8] where \( \text{R} \) belongs to the whole Rare Earth series. The purpose of the present paper is to apply a similar theoretical analysis to 3d-XPS spectra in \( \text{R(OH)}_3 \) compounds and to extend it to 2p-XAS spectra as well, in the same trihydroxide series. In section 2 we present our model study and the corresponding formalism for a systematic calculation of 3d-XPS and 2p-XAS spectra in \( \text{R(OH)}_3 \). The results of the calculations with \( \text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd} \) and \( \text{Sm} \) as well as the analysis of the experimental data are given in section 3, pointing out (as already mentioned) a coherence problem, as for the data on the 3d-XPS spectrum in \( \text{Ce(OH)}_3 \). In section 4 we discuss this questionable case, propose a theoretical prediction of the 3d-XPS spectrum and show some new preliminary measurements on it.

2. Formalism.

The Hamiltonian \( H_0 \) describing the initial state of the system is given by [2-3]:

\[
H_0 = \sum_{k, \nu} \varepsilon_{\nu}(k) a_{k\nu}^+ a_{k\nu} + \varepsilon_f \sum_{\nu} a_{f\nu}^+ a_{f\nu} + U_{ff} \sum_{\nu, \nu'} a_{f\nu}^+ a_{f\nu} a_{f\nu'}^+ a_{f\nu'} + \frac{V}{\sqrt{N}} \sum_{k, \nu} (a_{k\nu}^+ a_{f\nu} + a_{f\nu}^+ a_{k\nu}),
\]

where \( \varepsilon_{\nu}(k) \) is the energy of the valence band with the index \( k (=1, \ldots, N) \) specifying the energy levels, \( \varepsilon_f \) is the 4f level, \( U_{ff} \) is the Coulomb interaction between 4f electrons and \( V \) is the hybridization between 4f and valence states. The operator \( a_{i\nu} \) \( (i = k, f) \) represents the annihilation of an electron in the state \( (i, \nu) \) where \( \nu \) is the index specifying both spin and orbital degeneracy \( (\nu = 1, \ldots, N_f) \) with \( N_f = 14 \). In the final state of 3d-XPS, a core hole is
created and the 4f level is pulled down by the core hole potential. Therefore, the Hamiltonian is given by:

$$H = H_0 - U_{fc} \sum \nu a_{\nu}^+ a_{\nu},$$

(2.2)

where $- U_{fc}$ is the core hole potential acting on the 4f electron. The spectrum of 3d-XPS is represented by:

$$F_{\text{XPS}}(E_B) = \sum_f |\langle f|g \rangle|^2 \frac{\Gamma/\pi}{(E_B - E_f + E_g)^2 + \Gamma^2},$$

(2.3)

where $|g \rangle$ is the ground state of $H_0$ with energy $E_g$, and the $\{ |f \rangle \}$'s are the eigenstates of $H$ with energies $\{ E_f \}$; $E_B$ is the binding energy and $\Gamma$ denotes the spectral broadening corresponding to the lifetime of the core hole, as well as the experimental resolution. As far as 2p-XAS is concerned, a core electron is photo-excited to the Rare Earth 5d band, so that the final state is described by the Hamiltonian [3, 4, 6]

$$H_{\text{XAS}} = H_0 + \sum_k \epsilon_d(k) a_{dk}^+ a_{dk} - U_{fc} \sum \nu a_{\nu}^+ a_{\nu} + \frac{U_{fd}}{N} \sum_{k,k',\nu} a_{\nu}^+ a_{\nu}^+ a_{dk}^+ a_{dk'} - \frac{U_{dc}}{N} \sum_{kk'} a_{dk}^+ a_{dk'},$$

(2.4)

where the photo-excited 5d electron is assumed to couple with the 4f electron through an interaction $U_{fd}$ and with the core hole through the potential $- U_{dc}$. The corresponding absorption spectrum is expressed as:

$$F_{\text{XAS}}(\omega) = \frac{1}{N} \sum_f \left| \langle f|\sum_k a_{dk}^+ |g \rangle \right|^2 \frac{\Gamma/\pi}{(\omega - E_f + E_g)^2 + \Gamma^2},$$

(2.5)

$\omega$ being the energy of the incoming photon.

The Hamiltonians $H_0$, $H$ and $H_{\text{XAS}}$ are numerically diagonalized in the subspace of $4 f^n$, $4 f^{n+1} v$ and $4 f^{n+2} v^2$ configurations ($v$ being a hole in the valence band and $n = 0, 1, 2, ...$ respectively for La, Ce, Pr...) for a finite system where $\epsilon_v(k)$ and $\epsilon_d(k)$ are expressed as:

$$\epsilon_v(k) = \epsilon_v^0 + \frac{W}{2N} (2k - N - 1),$$

(2.6)

$$\epsilon_d(k) = \epsilon_d^0 + \frac{W_d}{2N} (2k - N - 1) (k = 1, ..., N).$$

(2.7)

Here $W$ and $W_d$ respectively represent the widths of the valence and conduction bands. The ground states to diagonalize the Hamiltonian for the initial and final states of 3d-XPS are given by $|f^n \rangle$, $|f^{n+1} v(k) \rangle$ and $|f^{n+2} v(k_1, k_2) \rangle$ [8] where $|f^n \rangle$ is the ground state of the $4 f^n$ configuration written as:

$$|f^n \rangle = \prod_{\nu = \nu_1}^{\nu_n} a_{\nu}^+ |f^n \rangle,$$

(2.8)

with $|f^n \rangle$ denoting the state in which the valence band is filled and the 4f level is empty, and the indices $\nu_1, ..., \nu_n$ are chosen arbitrarily from the $N_f$ indices. Then the state $|f^n \rangle$ is coupled through $V$ with the $4 f^{n+1} v$ configuration given by:

$$|f^{n+1} v(k) \rangle = \sqrt{\frac{1}{N_f - n}} \sum_{\nu \neq \nu_1, ..., \nu_n} a_{\nu}^+ a_{kv} |f^n \rangle.$$

(2.9)
Finally the state $|\psi^{n+1}\rangle$ is further coupled through $V$ with the following states in the 4 $\gamma^2$ configurations:

$$\left|\psi^{n+2}, \psi(k_1, k_2)\right> = \sqrt{\frac{2}{(N_f-n)(N_f-n-1)}} \sum_{\nu, \nu' \neq \nu_1 \ldots \nu_n} a_{k\nu}^+ a_{k_1\nu_1}^+ a_{k\nu'}^- |\psi^n\rangle \quad \text{(for } k_1 = k_2)$$

$$\sqrt{\frac{1}{(N_f-n)(N_f-n-1)}} \sum_{\nu, \nu' \neq \nu_1 \ldots \nu_n} a_{k\nu}^+ a_{k_1\nu_1}^+ a_{k_2\nu[]}^- |\psi^n\rangle \quad \text{(for } k_1 \neq k_2). \quad (2.10)$$

The matrix elements of $H_0$ and $H$ are given by:

$$\langle \psi^n | H | \psi^n \rangle = E_n = N_f \sum_k \epsilon_k(k) + n \bar{\epsilon}_f + \frac{n(n-1)}{2} U_{ff}, \quad (2.11)$$

$$\langle \psi^{n+1}, \psi(k) | H | \psi^{n+1}, \psi(k) \rangle = E_n + \bar{\epsilon}_f - \epsilon_k(k) + n U_{ff}, \quad (2.12)$$

$$\langle \psi^{n+2}, \psi(k_1, k_2) | H | \psi^{n+2}, \psi(k_1, k_2) \rangle = E_n + 2 \bar{\epsilon}_f - \epsilon_k(k_1) - \epsilon_k(k_2) + (2n+1) U_{ff}, \quad (2.13)$$

$$\langle \psi^{n+1}, \psi(k) | H | \psi^n \rangle = V \sqrt{\frac{(N_f-n)}{N}}, \quad (2.14)$$

$$\langle \psi^{n+2}, \psi(k_1, k_2) | H | \psi^{n+1}, \psi(k) \rangle = \begin{cases} \delta_{k_1, k_1} V \sqrt{\frac{2(N_f-n-1)}{N}} & \text{(for } k_1 = k_2) \\ (\delta_{k_1, k_1} + \delta_{k_2, k_2}) V \sqrt{\frac{(N_f-n-1)}{N}} & \text{(for } k_1 \neq k_2) \end{cases}, \quad (2.15)$$

where $H = H_0$ and $\bar{\epsilon}_f = \epsilon_f$ for the XPS initial state and $\tilde{H} = H$ and $\bar{\epsilon}_f = \epsilon_f - U_{fc}$ for the final state.

As regards the final state of 2p-XAS, we add a 5d electron to that of XPS, so that the ground states are:

$$|f^n, d(k)\rangle = a_{dk}^+ |f^n\rangle, \quad (2.16)$$

$$|f^{n+1}, \psi(k), d(k')\rangle = a_{dk'}^+ |f^{n+1}, \psi(k)\rangle, \quad (2.17)$$

$$|f^{n+2}, \psi(k, k'), d(k'')\rangle = a_{dk''}^+ |f^{n+2}, \psi(k, k')\rangle. \quad (2.18)$$

The matrix elements of $H_{XAS}$ are expressed as

$$\langle f^n, d(k) | H_{XAS} | f^n, d(k') \rangle = [\langle f^n | H | f^n \rangle + \epsilon_d(k)] \delta_{k, k'} + (nU_{fd} - U_{dc})/N, \quad (2.19)$$

$$\langle f^{n+1}, \psi(k_1), d(k) | H_{XAS} | f^{n+1}, \psi(k_1) \rangle = [\langle f^{n+1}, \psi(k_1) | H | f^{n+1}, \psi(k_1) \rangle + \epsilon_d(k)] \delta_{k, k'} + [(n + 1) U_{fd} - U_{dc})/N, \quad (2.20)$$

$$\langle f^{n+2}, \psi(k_1, k_2), d(k) | H_{XAS} | f^{n+2}, \psi(k_1, k_2) \rangle = [\langle f^{n+2}, \psi(k_1, k_2) | H | f^{n+2}, \psi(k_1, k_2) \rangle + \epsilon_d(k)] \delta_{k, k'} + [(n + 2) U_{fd} - U_{dc})/N, \quad (2.21)$$

$$\langle f^{n+1}, \psi(k), d(k) | H_{XAS} | f^n \rangle = \langle f^{n+1}, \psi(k_1) | H | f^n \rangle \delta_{k, k'}, \quad (2.22)$$

$$\langle f^{n+2}, \psi(k_1, k_2), d(k) | H_{XAS} | f^{n+1}, \psi(k_3) \rangle = \langle f^{n+2}, \psi(k_1, k_2) | H | f^{n+1} \psi(k_3) \rangle \delta_{k, k'}. \quad (2.23)$$
These results are for example a straightforward extension of those for La compounds \( (n = 0) \) given in [6] to arbitrary values of \( n \).


The experimental data [5] of 3d-XPS spectra in \( \text{R(OH)}_3 \) compounds for \( \text{R} = \text{La}, \ldots \text{Sm} \) are shown in figure 1. The analysis of these data is made in the same manner as the analysis in reference [8] and the results are shown from figure 2a to figure 2e. The parameter values estimated from this analysis are listed in table I and the changes of

\[
\begin{align*}
\Delta &= \epsilon_t - \epsilon^0_t + nU_{it}, \\
\Delta_t &= \Delta - U_{it}, \\
V_{\text{eff}} &= \sqrt{N_t - n} V,
\end{align*}
\]  

for various Rare Earth elements are plotted in figures 3 and 4. It is found that all the parameters, except \( V_{\text{eff}} \) for Ce, change rather smoothly with the change of \( n \) (i.e. the Rare
Fig. 2. — Calculated 3d-XPS spectra (full line) in R(OH)₃ compounds for R = La(a); Ce(b); Pr(c); Nd(d) and Sm(e). The intensity is expressed in arbitrary units. The experimental data of figure 1 are reported by dashed lines. Also the necessary background (to adjust theory with experiment) is indicated at the bottom of each spectrum; it is calculated by using equation (3.2) of reference [8], except for Sm(OH)₃ where it is taken as a straight line. However the detailed description of how to take the background does not seem to be so important.

Earth element). The value of $V_{\text{eff}}$ for Ce is anomalously large. We shall come back to this point.

By using the parameter values of table I, we also analyse the 2p-XAS observed by Beaurepaire et al. [1] and shown in figure 5 for R(OH)₃ compounds with R = La, Ce and Sm.
Table I. — *List of the parameter values estimated from the analysis of the 3d-XPS spectra in R(OH)₃ compounds with R = La, Ce, Pr, Nd and Sm; in the last line the deduced calculated values of n_f (the number of f electrons on the R ion) are reported.*

<table>
<thead>
<tr>
<th></th>
<th>La(OH)₃</th>
<th>Ce(OH)₃</th>
<th>Pr(OH)₃</th>
<th>Nd(OH)₃</th>
<th>Sm(OH)₃</th>
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<tr>
<td>Δ (eV)</td>
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<td>13.30</td>
<td>11.70</td>
<td>10.60</td>
<td>8.50</td>
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<tr>
<td>Δ_f (eV)</td>
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<td>1.10</td>
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<td>-1.40</td>
<td>-3.50</td>
</tr>
<tr>
<td>U_{ff} (eV)</td>
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<td>10.80</td>
<td>10.60</td>
<td>10.70</td>
<td>10.50</td>
</tr>
<tr>
<td>V_{eff} (eV)</td>
<td>1.72</td>
<td>3.35</td>
<td>1.39</td>
<td>1.49</td>
<td>0.90</td>
</tr>
<tr>
<td>W (eV)</td>
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<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Γ (eV)</td>
<td>1.30</td>
<td>1.60</td>
<td>1.70</td>
<td>2.00</td>
<td>2.50</td>
</tr>
<tr>
<td>n_f</td>
<td>0.02</td>
<td>1.06</td>
<td>2.01</td>
<td>3.02</td>
<td>5.01</td>
</tr>
</tbody>
</table>

Fig. 3. — Charge transfer energies in the initial (Δ) and final (Δ_f) states along the Rare Earth series for R(OH)₃ compounds with R = La, ... Sm. See equations (3.1) and (3.2) for the definitions and table I for the explicit values of the parameters.

Fig. 4. — Effective hybridization V_{eff} (Eq. (3.3) and Tab. I) along the Rare Earth series for R(OH)₃ compounds with R = La, ... Sm.
In our analysis, we assume that the core hole potential $U_{fc}$ is the same whenever arising from a 3d (like in 3d-XPS) or a 2p (like in 2p-XAS) core hole. The width of the 5d conduction band is fixed at $W_d = 6$ eV and the values of $U_{fd}$ and $U_{dc}$ which have been introduced in Hamiltonian (2.4) are then varied as adjustable parameters. The value of $\Gamma$ is also adjusted appropriately.

The result for La(OH)$_3$ is shown in figure 6a and b. In figure 6b the calculated $F_{XAS}(\omega)$ is shown for $(U_{fd}, U_{dc}) = (0$ eV, $0$ eV), $(2$ eV, $3$ eV) and $(4$ eV, $5$ eV). It is found that $F_{XAS}(\omega)$ depends strongly on $U_{fd}$ and $U_{dc}$. The result for $(U_{fd}, U_{dc}) = (4$ eV, $5$ eV) is in very good agreement with the experimental data as shown in figure 6a, where the background
is taken into account by convoluting $F_{\text{XPS}}(E_B)$ with a step function. For the treatment of the background contribution, see [9].

The results for Ce(OH)$_3$ and Sm(OH)$_3$ are shown in figure 7 and figure 8, respectively. The most striking fact found from this analysis is that, in order to reproduce the experimental 2p-XAS of Ce(OH)$_3$, we must assume anomalously large values of $U_{fd}$ and $U_{dc}$, as seen from figure 7a and b. According to the analysis of 2p-XAS so far made for LaF$_3$, La$_2$O$_3$, CeO$_2$, CeF$_4$, etc., the values of $(U_{fd}, U_{dc})$ are always around $(4 \text{ eV}, 5 \text{ eV})$ [3, 4, 6, 9]. Therefore, the results of our analysis for La(OH)$_3$ and Sm(OH)$_3$ are reasonable, but that for Ce(OH)$_3$ is strange. If we use $(U_{fd}, U_{dc}) = (4 \text{ eV}, 5 \text{ eV})$, for Ce(OH)$_3$, we have a satellite on the higher energy side of the 2p-XAS main peak, in disagreement with experiment. The anomalously large values of $U_{fd}$ and $U_{dc}$ correspond to the anomalously large value of $V_{\text{eff}}$. This is indispensable to reproduce the 3d-XPS of Ce(OH)$_3$ by Tatsumi et al. [5].

With the above results in mind, we would like to point out a possibility that the

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![Fig. 7.](image)  
Fig. 7. — Calculated 2p-XAS spectra for Ce(OH)$_3$ compounds (with $\Gamma = 2 \text{ eV}$) and expressed in arbitrary units, (a) for $(U_{fd}, U_{dc}) = (8 \text{ eV}, 9 \text{ eV})$ and using the background shown at the bottom of the figure — the corresponding experimental data has been drawn with a dotted line; (b) for $(U_{fd}, U_{dc}) = (0 \text{ eV}, 0 \text{ eV})$ (1); $(4 \text{ eV}, 5 \text{ eV})$ (2); $(6 \text{ eV}, 7 \text{ eV})$ (3) and $(8 \text{ eV}, 9 \text{ eV})$ (4).

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![Fig. 8.](image)  
Fig. 8. — Calculated 2p-XAS spectra for Sm(OH)$_3$ compounds (with $\Gamma = 2 \text{ eV}$) and expressed in arbitrary units, (a) for $(U_{fd}, U_{dc}) = (3 \text{ eV}, 4 \text{ eV})$ and using the background shown at the bottom of the figure — the corresponding experimental data has been drawn with a dotted line; (b) for $(U_{fd}, U_{dc}) = (0 \text{ eV}, 0 \text{ eV})$ (1); $(1 \text{ eV}, 2 \text{ eV})$ (2); $(2 \text{ eV}, 3 \text{ eV})$ (3) and $(3 \text{ eV}, 4 \text{ eV})$ (4).
experimental data of 3d-XPS of Ce(OH)$_3$ [5] might not be intrinsic. For example, the data might be much influenced by some impurity phase, different from Ce(OH)$_3$, on the surface of the sample. Now, we assume that the value of $V_{\text{eff}}$ of genuine Ce(OH)$_3$ is obtained by an interpolation between the values for La(OH)$_3$ and Pr(OH)$_3$ (so that $V_{\text{eff}} = 1.5$ eV). Then we calculate 3d-XPS with this value of $V_{\text{eff}}$ and obtain the result shown in figure 9. Furthermore, when we analyse the 2p-XAS of Ce(OH)$_3$ with $V_{\text{eff}} = 1.5$ eV, as shown in figure 10, we can obtain a good agreement with the experimental data with reasonable values of $U_{\text{fd}}$ and $U_{\text{dc}}$ ($U_{\text{fd}} = 5$ eV, $U_{\text{dc}} = 6$ eV).
CeO$_2$ compounds: in particular, figure 11b is quite comparable — in relative intensities and energy spacing of the peaks — with figure 1b, wrongly attributed to Ce(OH)$_3$. On the contrary the energy spacing of the peak positions in figure 11a is smaller (of the order of magnitude of about 3 eV) and therefore in agreement with our theoretical prediction of figure 9. As a conclusion it would be very interesting and important to reexamine more precisely the 3d-XPS spectra of clean Ce(OH)$_3$ samples and confirm whether the present conclusion is actually correct.

Acknowledgments.

The authors would like to thank Dr. F. Le Normand for providing the sample of Ce(OH)$_3$ used to obtain the preliminary results of figure 11. Part of the present paper was prepared during a short stay of one of the authors (A.K.) at the University Louis Pasteur, and he would like to thank the members of IPCMS for warm hospitality; he also thanks Dr. K. Okada for valuable discussion.
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