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XPS investigations on cesium uranates: mixed valency behaviour of uranium

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Abstract

Several pure cesium uranate phases were prepared ($Cs_2U_2O_7$, $Cs_2U_4O_{13}$, $Cs_2U_4O_{12}$, $Cs_4U_5O_{17}$) and measured with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Detailed XPS scans of the main photoelectron peaks (U 4f, Cs 3d, O 1s and valence band) were made. Peak positions, peak widths and satellite positions were measured and compared between the uranates. A systematic shift in the position of the U 4f lines was found to be correlated with the Cs/U ratio. The mixed valency behaviour of uranium was observed and studied. Interpretation of the satellite structure of the U 4f peaks and the deconvolution of these peaks have been used to quantify the chemical states of uranium present in the mixed valency compound $Cs_2U_4O_{12}$. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The physico-chemical behaviour of fission products in nuclear fuel during and after irradiation has been studied extensively during the past decades. In spite of the large amount of chemical, crystallographic and thermodynamic data available, the knowledge on the very complicated UO_2-fission product system is still far from complete. In this paper, the multivalent character of uranium in cesium uranates will be assessed by a systematic X-ray photoelectron spectroscopy (XPS) study of a series of cesium uranates.

Cesium is generally considered to be an important, yet peculiar fission product in view of its high fission yield, its high reactivity with and mobility in nuclear fuel and its relatively long half-life (~30 yr for ^{137}Cs). Its mobility in a UO_2 matrix is studied in relation to final disposal [1], interim storage of spent fuel [2], environmental issues in case of severe accidents [3,4] and changes in physical properties of fuel pins during service operation [5,6]. Although the environmental parameters (mainly temperature and oxygen potential) differ for the above-mentioned domains, the mechanisms that govern cesium migration inside the oxide fuel are a common interest. In the study of migration of fission products, the chemical valence of uranium is considered to be an important parameter. The diffusion coefficients are known to depend strongly on the fuel stoichiometry and hence on the local uranium valency (e.g. the uranium diffusion coefficient in fuel changes five orders of magnitude when going from $UO_{2.00}$ to $UO_{2.10}$) [7]. The influence of cesium on this valency being important, an XPS investigation on the chemical valency of uranium in cesium uranates was performed.

The valence state of uranium has been studied before in simple uranium oxides [8,9] (UO_2, U_3O_8, U_4O_9, UO_3,...) as well as in alkali and alkaline earth uranates [10–12] (Na–U–O, Li–U–O,... systems). Due to the multivalent character of uranium (U^{III} in some organic phases, U^{IV}, U^{V} and U^{VI} are possible oxidation states of uranium), it is often not a straightforward task to determine the valence state of uranium in its compounds. XPS is in principle capable of discerning the different oxidation states. Although several uranate systems have been investigated by XPS, a systematic study of the

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uranium valence in cesium uranates has not yet been performed.

It is well-known [8,9,12–14] that both the position of the U 4f core lines and the shake-up satellites at the high binding energy side of the same U 4f lines are affected by the valence state of uranium. The chemical shift of the U 4f core lines between U^{IV} and U^{VI} is of the order of 1.7 eV [8]. Since the FWHM of the U 4f lines is of the order of 2 eV, mixed valency compounds will show broad main peaks that present the convoluted signal of the respective valencies [10]. Shake-up satellites are small peaks (5–10% of the intensity of the main peak in this case) that are produced by photoelectrons that have lost part of their initial energy to a valence band electron. When a photoelectron is created, the valence electrons experience an electrostatic potential [14,15]. Via the electrostatic field, part of the energy of the photoelectron may be lost to an electron in the metal-oxygen bonding band to transfer it to an empty or partially filled energy level. The energy difference between these latter levels defines the difference in position between the satellite peak and the photoelectron peak to which it is associated. Since changes in valency have their effect on the valence band and the conductance band, they will show up in the satellite structure as well. For uranium, both U 4f core level peaks show a satellite at 6 eV for U^{IV}, at 8 eV for U^{V} and two satellites, one at 4 eV and the other at 10 eV for U^{VI} [16]. The shake-up satellite positions are always expressed relative to the associated photoelectron peak position.

2. Experimental

2.1. Preparation

From an examination of the ternary Cs–U–O system in Fig. 1 [17], we can see that the only uranates in equilibrium with UO_2 are $Cs_2UO_{3.56}$ [18,19], Cs_2UO_4 and $Cs_2U_4O_{12}$, but should no equilibrium be reached, $Cs_2U_2O_7$ can be formed as well. One must keep in mind the low oxygen potential in the fuel and the high temperatures involved, at least during normal operation. In the present study, we focus on the XPS analysis of $Cs_2U_2O_7$, $Cs_4U_5O_{17}$ $Cs_2U_4O_{13}$ and $Cs_2U_4O_{12}$. Due to the highly hygroscopic nature of Cs_2UO_4, it was not yet included in the XPS study. Nobody has yet prepared $Cs_2UO_{3.56}$ in pure form and its crystallographic properties are currently unknown [17].

The preparation of cesium uranates has been studied in the past [20,21]. Perhaps the most elaborate study of the crystallographic aspects of the Cs–U–O system has been performed by Van Egmond [22]. In the abovementioned study, a pseudo-binary phase diagram for the Cs_2O–UO_2-system was proposed. Part of this diagram is reproduced in Fig. 2. We have prepared the samples by heating carefully ground mixtures of cesium carbonate (Cs_2CO_3, Merck, 99.99% pure) and U_3O_8. The atomic ratios Cs/U were fixed in the starting mixture by precise weighing of the reaction powders. Since Cs_2CO_3 is hygroscopic, we have stored the carbonate in a dry atmosphere in a glove box and have taken out only small quantities when necessary, thus trying to avoid as much as possible the errors introduced during the weighing.

The preparation conditions and description of the uranates are reproduced in Table 1. The cesium carbonate decomposes at relatively low temperatures (around 400°C) into CO_2 and Cs_2O. The CO_2 escapes and the two remaining oxides Cs_2O and U_3O_8, react. Which uranate is formed depends on the Cs/U ratio in the initial mixture, the temperature and the oxygen

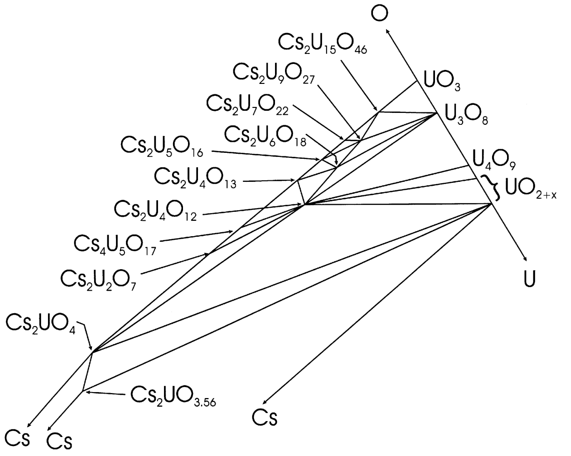

Fig. 1. Isothermal section of the ternary diagram of the Cs–U–O system (after [17]). Notice the tie lines between UO_2 and $Cs_2U_4O_{12}$, Cs_2UO_4 and $Cs_2UO_{3.56}$.

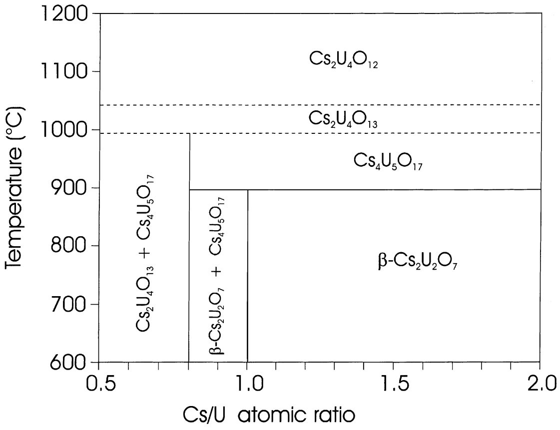

Fig. 2. Section of the pseudo-binary representation of the Cs–U–O system to visualize the temperature domains of existence of the uranates in open atmosphere [22].

Table 1
Preparation parameters of the uranates (the Cs/U ratio was determined by ICP-MS, which also proved that the total impurity level was always below 1000 ppm)

XRD	Cs/U	T (°C)	Atmosph.	Time (h)
$Cs_2U_2O_7$	0.96	800	Air	48
$Cs_2U_4O_{13}$	0.48	800	Air	72
$Cs_2U_4O_{12}$	0.48	1100	CO_2	12
$Cs_4U_5O_{17}$	0.78	800	Air	72

potential [22,23]. Except for $Cs_2U_4O_{12}$, the mixtures were heated in open atmosphere at the appropriate temperature, deduced from the pseudo-binary phase diagram (Fig. 2). The preparation of $Cs_2U_4O_{12}$ was performed at a reduced oxygen potential to avoid the need for quenching and to promote the formation of $Cs_2U_4O_{12}$ in favour of $Cs_2U_4O_{13}$. To reduce the oxygen potential of the atmosphere, UO_2 powder was placed in the furnace in separate containers along with the mixture. Because of the high affinity of UO_2 for oxygen, the powder served as an oxygen getter. As can be seen in Fig. 3, at 1100°C the formation of UO_{2+x} ($x \sim 0.01$) is favoured to the formation of $Cs_2U_4O_{13}$ (which is situated at higher oxygen potentials) while the formation of $Cs_2U_4O_{12}$ proceeds [17]. After the preparation, the UO_2 powder was measured with XRD and was proven to be partially oxidized. Furthermore, preparation attempts afterwards without the powder present, gave less satisfying results. Homogeneity and phase formation were verified by X-ray diffraction (XRD). The positions of the XRD lines were compared with structure results as determined by Van Egmond [22]. We have found that the prepared uranates were pure. Line intensities measured in this study do not agree completely with previous results from 1976 as found in the JCPDS-database (compounds 29-0429 to 29-0442), as was already remarked by Takano et al. [24]. The accuracy of today's detectors is superior to what could be obtained on Guinier exposures, which explains this discrepancy. Currently, we are exploiting the XRD data to refine the crystal structures [25].

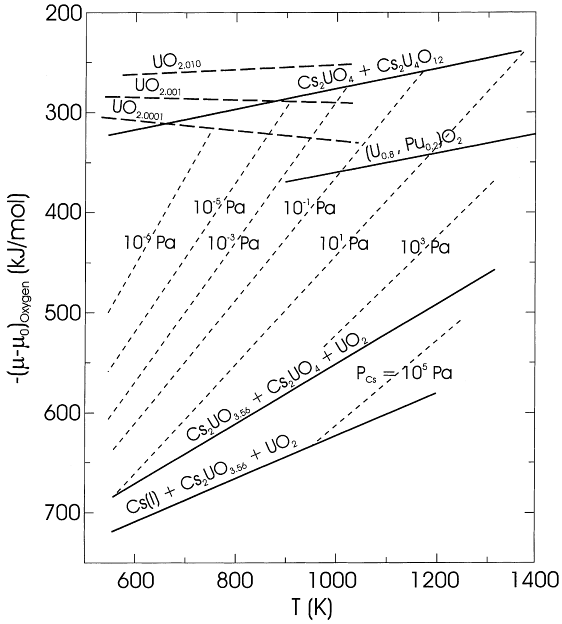

Fig. 3. Ellingham diagram of the Cs–U–O and UO_{2+x} system for compositions between Cs and $Cs_2U_4O_{12}$. $Cs_2U_4O_{13}$ is above the scale and hence above UO_{2+x}, which makes UO_2 a suitable oxygen pump for the preparation of $Cs_2U_4O_{12}$ [17].

We also verified the purity of our samples by mass spectrometry, to determine the Cs/U ratio for comparison with the formula obtained from the XRD spectra and to assess the contamination with impurities. The samples showed a small (4%), but systematic deficiency in Cs, which is to be expected because of the volatility of Cs_2O. However, no U_3O_8 has been detected in the XRD spectra. The concentrations of foreign elements in the samples are far below the detection limit of the XPS or XRD.

2.2. Spectral acquisition and processing

For the XRD measurements, a Siemens D5000 was used for detailed scans of several hours (up to 2 days), while a Philips PW1050 diffractometer served to make fast 20 min scans. Both systems are equipped with the Siemens DIFFRAC AT or DIFFRAC+ software packages.

The instrument used for XPS measurements was a Physical Electronics ESCA Model 1600, with a non-monochromated Al X-ray source, operated at 400 W. The system is PC-controlled and the data were acquired over several hours (typical acquisition time: 8 h per compound) and analyzed with the PHI MULTIPAK package. No flood gun was used.

After preparation and XRD analysis of the cesium uranate powders, they were pressed into pellets and kept in dry conditions. Right before starting the XPS analysis, each pellet was broken and the fresh surface was mounted in the spectrometer. This approach proved to be appropriate for the uranates presented in this paper, but not for the highly hygroscopic Cs_2UO_4. Its affinity for water was no problem for the XRD analysis, but is incompatible with the UHV of the XPS spectrometer.

The spectra were acquired with a wide aperture (2 mm diameter) to boost the photoelectron yield, which enabled us to adopt low pass energy values (10 eV) to enhance spectral resolution, resulting in a theoretical energy resolution of 0.54 eV. These settings allowed the recording of high precision spectra, even for the low energetic valence spectrum. For the latter, the pass energy was set to 23 eV and recording times of several hours were used. The spectra were checked with UPS and basically the same features were found. Because of the higher resolution that could be obtained in XPS-mode, the UPS spectra are not displayed here. Initial processing of the XPS spectra includes the removal of X-ray satellites produced by higher characteristic X-rays of the Al anode and correction for surface charging that occurs for these insulators.

The charging correction was deliberately *not* made on the basis of a gold coating, since the position of the gold peak depends on the dimension of the gold islands, the substrate, etc. [26]. Instead, we have shifted all spectra, including those of UO_2, to reposition the C1s peak at 284.6 eV [27]. In most reports on UO_2, it is stated that no charging correction is necessary because of the relatively good conductivity of this semi-conductor. However, in our case, comparison between experimental results on UO_2 and on cesium uranates is only possible when both spectra are on the same scale and accurately calibrated. Since the electrical conductivity of the cesium uranates is very poor, only by using binding energy values relative to a peak that is insensitive to sample preparation and composition, adequate comparisons can be made. In our XPS measurements, slight carbon contamination is present on the sample surface, originating from hydrocarbons. The C1s photoelectron peak position of this type of contamination can be considered independent of the sample, when no reaction between the carbon and the substrate is involved and when surface contamination is limited (as in our case). Although a variety of values for the adventitious C1s position have been reported (from 284.6 to 285.2 eV [15]), the C1s binding energy adopted for correction is of less importance, while the reporting of the measured value is vital.

After removal of the background (iterated Shirley background), fitting of the U $4f_{7/2}$ peaks was performed using mixed Gaussian–Lorentzian peaks. The U $4f_{5/2}$ peaks were not included because of the interference with the 10 eV satellite from the U $4f_{7/2}$ peak. The pure U^{VI} compounds were fitted first and the determined peak parameters were used to deconvolute the peaks from the mixed valency compound. Restrictions were imposed on the parameters (FWHM and % Gaussian) of the composing peaks, using the knowledge of the peak parameters obtained for the monovalent compounds. The fitting software was programmed to avoid large digressions from the peak parameters obtained on the monovalent compounds.

3. Results

3.1. Analysis of UO_2

The analysis of a pure UO_2 sample was performed for reference purposes. The results are shown in Table 2. The U $4f_{7/2}$ and U $4f_{5/2}$ peaks (Fig. 4(a)) are located at 379.5 and 390.3 eV, respectively. The main peak positions reported here are significantly lower (0.4–1.1 eV) than reported by others [13,9]. The separation between the two peaks however, is identical as reported previously. This suggests that the difference between our results and literature values is due to a difference in charging correction procedures. A comparison of the O 1s peak position recorded in the present analysis with the position reported by Allen et al. indeed confirms a systematic shift of about 0.7 eV.

The instrumental setting as applied in this study allowed us to obtain a FWHM of slightly less than 2 eV for both U 4f peaks in pure UO_2 (Table 2). This is slightly better than reported previously [13,9] and confirms that the sample, its preparation and the instrumental settings are appropriate for a detailed study of the U 4f line structure.

At the high binding energy side of both U 4f lines, a satellite is observed with an intensity of 15% of the main peaks (see Fig. 4(a)). The energy difference between the satellite and its associated main peak is 6.7 eV and the satellite width is 2.6 eV (FWHM). Both positions and intensities of the observed satellite peaks are in accordance with reported values [9].

Table 2
Numerical results of the peak positions in the XPS spectra (all positions and widths are in eV and have been corrected for charging. The satellite positions are expressed as an energy difference to the respective (U $4f_{5/2}$) main peak. α_3 is a value that expresses the skewness of the O 1s peak. Values of $\alpha_3 > 0$ indicate a skewness towards high energy values

U val.	Compound	Uranium					Oxygen		Cesium	
		U $4f_{7/2}$	U $4f_{5/2}$	FWHM	Sat.	FWHM	O 1s	α_3(O 1s)	Cs $3d_{5/2}$	FWHM
IV	UO_2	379.5	390.3	2.0	6.7	2.6	529.6	n/a	n/a	n/a
V/VI	$Cs_2U_4O_{12}$	380.1 (379.7 + 380.8)	390.9	2.4 (1.6 + 1.9)	9.0	4.4	529.3	1.26	723.7	1.9
VI	$Cs_2U_4O_{13}$	380.9	391.7	1.9	10.1	2.5	529.6	0.58	723.7	1.9
VI	$Cs_4U_5O_{17}$	380.7	391.5	1.9	10.3	2.7	529.4	0.89	723.6	1.9
VI	$Cs_2U_2O_7$	380.5	391.3	2.0	10.1	2.6	529.4	0.48	723.5	2.0

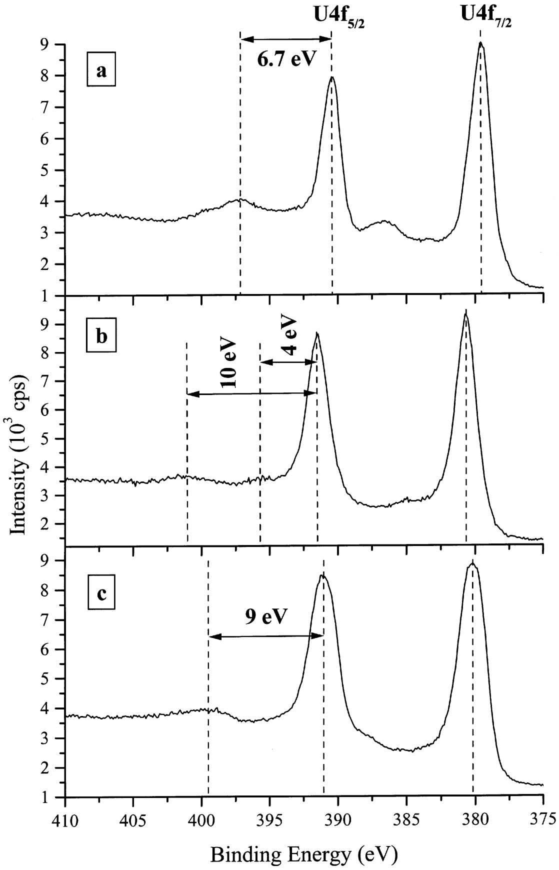

Fig. 4. Comparison of the U 4f peak position, shape and satellite structure for the different types of samples. The peak parameters for the U 4f peaks are detailed in Table 2: (a) U 4f spectrum of UO_2. A satellite is positioned at 6.7 eV distance from each main peaks; (b) Typical U 4f spectrum from a monovalent compound ($Cs_4U_5O_{17}$) with narrow U 4f peaks. The satellites are found at a distance of 10 eV and 4 eV from the main peak; (c) U 4f peaks of the mixed valency compound ($Cs_2U_4O_{12}$). Note the large FWHM compared to (b). A broad single satellite is found around 9 eV.

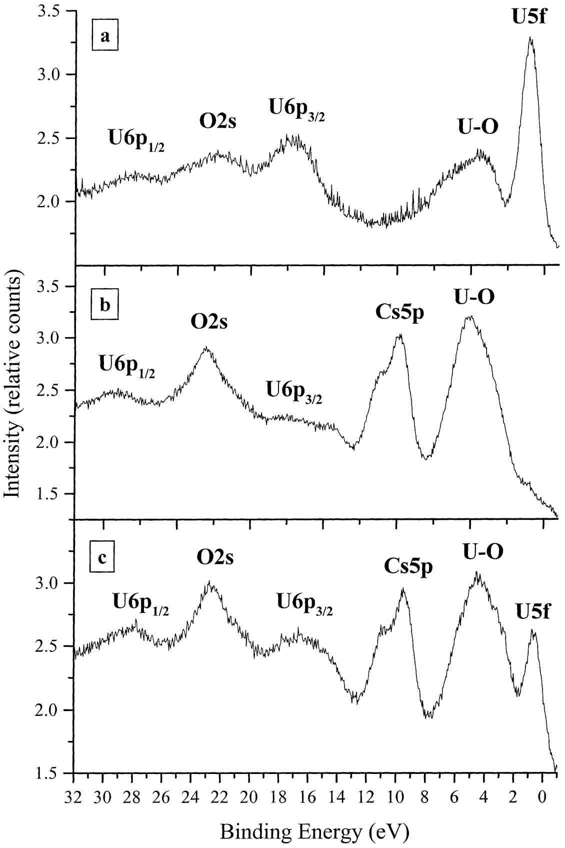

Fig. 5. Comparison of the valence band spectra for the different samples studied: (a) Valence band spectrum for UO_2. Notice the intense U $5f_{5/2}$ peak near the Fermi level; (b) Typical valence band of a monovalent cesium uranate ($Cs_4U_5O_{17}$). The absence of the U 5f peak witnesses the valence state VI for U; (c) Valence band of $Cs_2U_4O_{12}$. Observe the appearance of the U 5f peak for this mixed valency uranate, compared to (b).

In the valence band region (Fig. 5(a)) we mainly observe the U–O bonding band at about 4.5 eV, the O 2s peak at around 23 eV and the U 5f peak at 0.9 eV.

3.2. Monovalent (valency VI) compounds: $Cs_2U_2O_7$, $Cs_2U_4O_{13}$ and $CS_4U_5O_{17}$

We will first examine the pure U^{VI} compounds, for which the typical U 4f peaks are shown in Fig. 4(b). Binding energies, as well as FWHM and satellite positions of the U $4f_{7/2}$ and U $4f_{5/2}$ peaks are presented in Table 2. The peak parameters were obtained on the basis of the fitting procedure explained in Section 2.2 and are shown in Fig. 6(a). The major advantage of this approach was the fact that we had a direct check of the lineshape parameters, the most important being the percentage Gaussian and Lorentzian, and of the goodness-of-fit. In this way, artifacts such as instrumental instabilities are immediately recognized.

The peak positions for $Cs_2U_2O_7$ (380.5 and 391.3 eV) agree with previously published XPS data on this uranate (380.6 and 391.4 eV, after compensation for the difference in charging correction methods) [3], and the widths are slightly smaller in our case (2.0 eV compared to 2.4 eV), which is due to different experimental conditions. For $Cs_2U_4O_{13}$ and $Cs_4U_5O_{17}$, no XPS analyses have yet been published. Our results (Table 2) show that with increasing U/Cs ratio, the U 4f peak positions shift to higher binding energies: for $Cs_4U_5O_{17}$, the U $4f_{7/2}$ is found at 380.7 eV and U $4f_{5/2}$ at 391.5 eV, for $Cs_2U_4O_{13}$, the U $4f_{7/2}$ is at 380.9 eV and U $4f_{5/2}$ at 391.7 eV. This is in accordance with the fact that for UO_3, which is also a

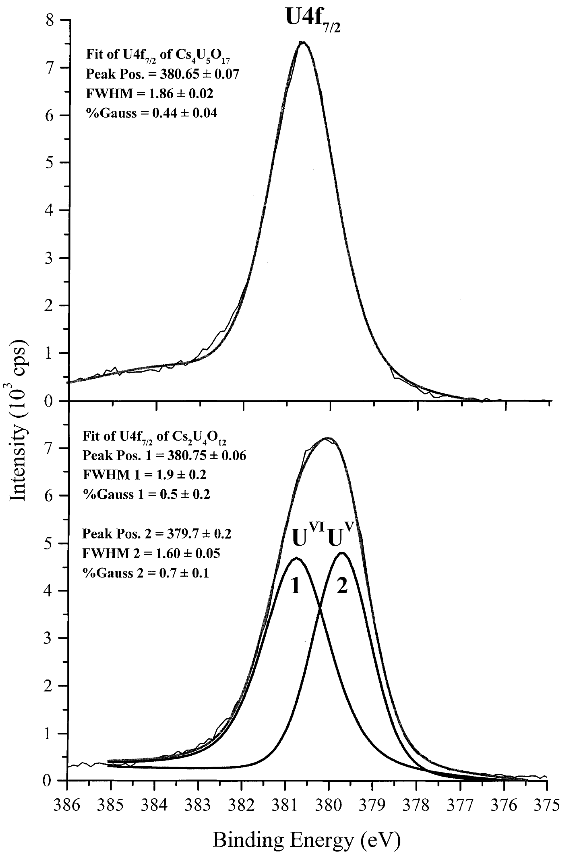

Fig. 6. Results of the fitting of the U 4f$_{7/2}$ peak of the uranates: (a) Cs$_4$U$_5$O$_{17}$ as an example of a monovalent compound; (b) Deconvolution of the U 4f$_{7/2}$ peak of Cs$_2$U$_4$O$_{12}$ showing the mixed valency of this compound. Numerical parameters of the fit are shown with the graphs.

U^{VI} compound, the U 4f core levels have still higher binding energies [9].

The satellite structure of these compounds, as seen in Fig. 7, is in agreement with published results for other U^{VI} compounds [12]. The satellite-peak separation is around 10 eV and we can clearly distinguish the 4 eV satellite, both of which are typical for U^{IV} photoelectron spectra. Note that the FWHM of the satellites is about 2.5 eV. The 10 eV satellite has found its explication in the charge transfer from the U–O bonding band to the empty U 6d conduction band, separated by 10 eV [10], while the 4 eV satellite is associated with the transition between the U–O bonding band and the empty U 5f level [14].

In the valence band spectra (Fig. 5(b)) of these compounds, the important features are the Cs 5p peaks that appear and the absence of the U 5f peak. The Cs 5p peaks at 9.5 eV show a distinct shoulder that is the onset of the separation between Cs 5p$_{1/2}$ and Cs 5p$_{3/2}$. The U 6p peaks, inherently low yield peaks, are obscured by the O 2s and Cs 5p peaks, which makes it impossible to observe possible splitting of the U 6p$_{3/2}$ peak by ligand electric fields [11].

3.3. Multivalent compound: Cs$_2$U$_4$O$_{12}$

Let us now go on to the case of Cs$_2$U$_4$O$_{12}$, which can be written as Cs$_2$ (U$_3^{VI}$U^{IV})O$_{12}$ or Cs$_2$(U$_2^{VI}$U$_2^{V}$)O$_{12}$. The U 4f peaks (Fig. 4(c)) are shifted by approximately 0.5 eV to the low binding energy side (380.1 and 390.9 eV), with respect to those for the pure U^{VI} compounds, because of the presence of different valencies. Although the peaks are very broad (2.4 eV), they are still symmetric, which indicates that the different valencies are present in equal amounts. Determination of the peaks from the individual valencies is done by deconvoluting the peak, as is shown in Fig. 6(b). The deconvoluted U 4f$_{7/2}$ peaks are found at 379.7 and 380.8 eV, implying a separation between the two peaks of 1.1 eV, which would be in agreement with a mixture of U^{VI} and U^{V}. We notice that the peak areas are practically the same, which confirms the 1:1 ratio we expect when U is present. Calculating from the area of the fitted curves, we would have 48% U^{V} and 52% U^{VI}. Attempts to fit the main peak using two curves with areas that have a 3:1 ratio (as would be the case if U^{IV} was present) all resulted in much higher χ^2-values.

The satellite structure of the U 4f peaks shows, as can be seen in the spectra in Fig. 7, the presence of a broad satellite (FWHM = 4.4 eV) around 9 eV separation, with a long tail on the high binding energy side. We can consider the satellite to be produced by a convolution between the 8 eV satellite from U^{V} and the 10 eV satellite from U^{VI}. A rough fitting of the satellite peak demonstrated that the satellite can be constructed by convoluting two peaks (at 8.4 eV and 10.9 eV distance from the main peaks). The satellite peak positions were determined with reference to their appropriate associated main peak, i.e. the 8.4 eV distance is with respect to the U^{V} main peak, while the 10.9 eV distance is referred to the U^{VI} peak. By fitting the satellite peak, we deduced the presence of another, very broad and weak satellite around 20 eV. Other weak, broad satellites at larger distances from the main peak have been reported before [10,13] and are attributed to energy loss processes (recorded by EELS) [14]. Note also the absence of the 4 eV satellite that was observed for the monovalent compounds.

We can observe the difference between the monovalent and multivalent compounds again in the valence band spectrum (Fig. 5(c)). We can clearly distinguish the U 5f peak, situated close to the Fermi level, which was absent for the monovalent compounds.

4. Discussion

Both position and satellite fine structure of the U 4f core level peaks are known to be sensitive to the

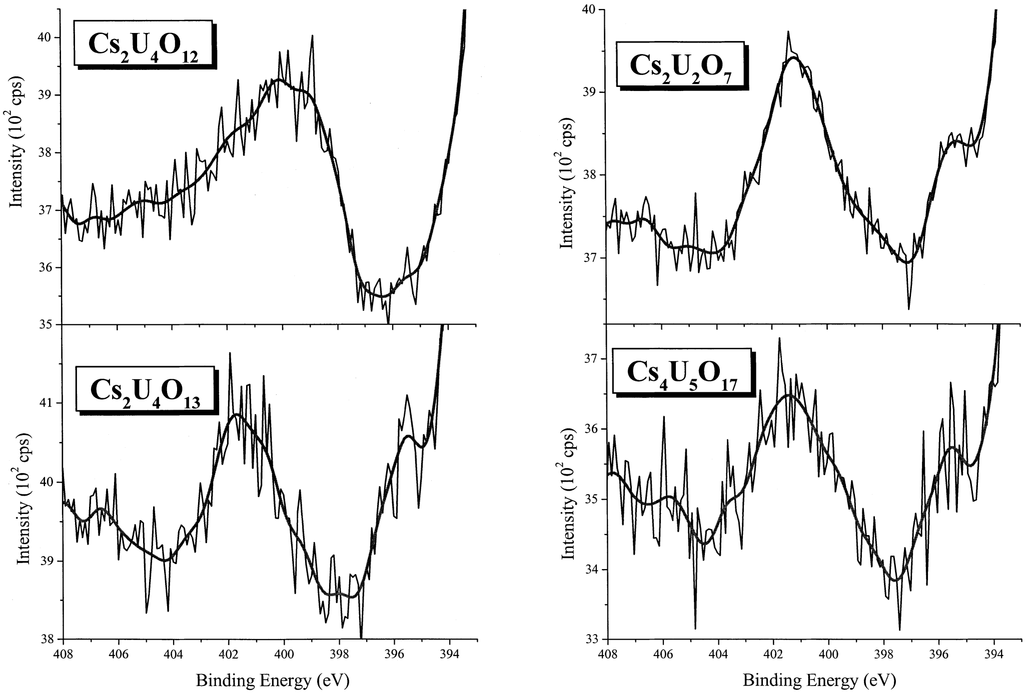

Fig. 7. Detailed view of the shake-up satellites of the U 4f peaks. FFT-smoothing has been applied to provide a better view of the satellite structure. Notice the difference between the monovalent compounds and the multivalent $Cs_2U_4O_{12}$. Both the satellite position and width are very different from the values found for the monovalent compounds (see Table 2). The disappearance of the 4 eV satellite for $Cs_2U_4O_{12}$ can also be observed.

uranium valency [8,9,12–14]. In this study, we have systematically analyzed a series of carefully prepared monophasic cesium uranates and a pure UO_2 sample, The cesium uranate series comprises three phases with uranium in valence state VI and one phase in which uranium is present in multiple valencies.

In order to be able to compare peak positions for different samples, charging corrections have to be carried out with great care, since the chemical shifts are minute. We based our charging correction procedure on the position of the C1s peak (284.6 eV). Although for pure UO_2, charging correction is not always necessary, we have applied the same correction procedure for UO_2 also, to ensure accurate comparison. As a consequence of the charging compensation as applied in this study, the peak positions of the U 4f lines recorded for UO_2 are lower than reported by other authors [13,26]. The O 1s line position for the same sample confirms that this shift is due to different charging correction procedures.

The chemical shift and lineshape analysis of the U 4f core level is based on the U $4f_{7/2}$ line. For UO_2, its position is 379.5 eV and its FWHM is 2.0 eV. The cesium uranate compounds with monovalent U^{VI} show an energy shift of the U $4f_{7/2}$ line of 1.0 to 1.4 eV with respect to UO_2. With decreasing Cs/U ratio, the line shift increases: for $Cs_2U_2O_7$ (Cs/U = 1), the U $4f_{7/2}$ is shifted by 1.0 eV, for $Cs_4U_5O_{17}$ (Cs/U = 0.8), the line shift is 1.2 eV and for $Cs_2U_4O_{13}$ (Cs/U = 0.5), it is 1.4 eV. This increase in line shift of the U 4f core level with increasing uranium oxide character is in accordance with the reported position of the core level for UO_3 (uranium valence VI, pure oxide), where the line shift with respect to the position in UO_2 (uranium valence IV) is still higher (1.7 eV [9]). It may thus be concluded that, although the peak position of the U 4f peaks is primarily determined by the uranium valency, other factors influence its position also.

The position of the U 4f line for the mixed valency compound $Cs_2U_4O_{12}$ (Cs/U = 0.5) is 390.9 eV, which is clearly different from the position of the same line in $Cs_2U_4O_{13}$ (with identical Cs/U ratio, but different valency), which is at 391.7 eV. The U 4f peak width for $Cs_2U_4O_{12}$ is also substantially larger (2.4 eV) than for all other samples (2.0 eV), which indicates the mixed uranium valency character of this compound. The deconvolution of the broad U $4f_{7/2}$ peak proved that $Cs_2(U^{V}_2U^{VI}_2)O_{12}$ is the correct formula representation of this phase.

The valency of uranium can also be assessed through the analysis of the satellite structure of the U 4f lines. Both U $4f_{7/2}$ and U $4f_{5/2}$ lines show the same satellite fine structure, but the U $4f_{7/2}$ satellites overlap with the

U $4f_{5/2}$ main peak. The analysis is therefore performed on the U $4f_{5/2}$ satellites. It is clear from Fig. 7 that the satellite structures provide an excellent way for qualitative differentiation between the uranium valencies in different cesium uranates. All compounds with uranium in valence state VI show a similar satellite structure (two separated satellites, one at 4 eV, the other at 10 eV). The satellite positions are in accordance with the reported values for other uranates with uranium in valence state VI [16]. For $Cs_2U_4O_{12}$, the satellite structure clearly is different, with only one broad satellite centered at 9 eV. Although curve fitting to shake-up satellite peaks is a very error-prone technique, one can indeed construct the broad satellite from two peaks. Uranium in valence state V yields a satellite at 8 eV, and U^{VI} has a satellite at 10 eV separation, which together indeed would produce a broad satellite centered at 9 eV. Satellite analysis however, should primarily be regarded as a fingerprinting tool and not be used for quantitative valency determinations. We also note that the satellite at 4 eV is absent in the mixed valency compound. The 4 eV satellite is observed in all uranates and uranium oxides with valence state VI, and similar as in our case, it has been reported to disappear in other mixed valency compounds too ($Rb_2U_4O_{11}$ [12] and substoichiometric UO_3 [28]). Conductance band spectroscopy will be performed in the future to elucidate this problem.

Next to the position and fine structure of the U 4f core lines, also the valence band region reflects changes in the uranium valency. The main difference between the valence band spectra for the different compounds, lies in the presence and intensity of the U $5f_{5/2}$ peak. In compounds where uranium assumes a pure valence state VI, the U 5f level is empty and the XPS spectra accordingly show no peak. The valence band spectrum of $Cs_2U_4O_{12}$ clearly shows the U 5f line, which proves the presence of uranium in a valence state lower than VI. An identification of the true oxidation state (V or IV), however, is not possible on the basis of the presence of this U 5f line since in both cases the same amount of 5f electrons contributes to the peak, i.e. one from each U^{V} or two from the U^{IV}. In UO_2, the U 5f line is of course also present, and its intensity is much higher than in $Cs_2U_4O_{12}$, which is expected. For some monovalent compounds, where no oxidation states other than VI are present, we see a small onset of the U 5f peak, which is due to the reduction of the surface in the spectrometer. In-situ reduction of the surface of uranium oxides and other uranates was reported also by Allen et al. [9,13,16]. The effect of the presence or absence of U 5f electrons has macroscopic influences as well. It can be remarked even before any spectral analysis, just by looking at the charging corrections necessary for the different uranates. The charging is a bulk phenomenon and is relatively insensitive to surface reduction. $Cs_2U_4O_{12}$ required considerably less charging correction (2.7 eV) compared to the others (around 6 eV), due to the proximity of the U 5f electrons to the Fermi level. In fact, visual observation also shows a difference between these types of uranates, since the mixed valency compounds are black, while the others have colors ranging from bright yellow to red-brown, which is also a consequence of the valence band structure.

It should be noted that the other peaks show little or no variation in peak shape or position. In the valence band spectra, one clearly sees the insensitivity of the O 2s peak and U–O bonding band positions. Also the intense Cs 3d peaks do not display measurable shifts in peak position or differences in peak shape for the different compounds. For future XPS analysis e.g. of irradiated fuel in which different cesium uranates along with many other fission products are expected to occur simultaneously, this is an important observation. While XPS might be a possible tool to probe for the chemical state of uranium, it will most probably not be possible to obtain much information on the chemical state of cesium, not to mention the determination of the uranate phase present.

Another peak from which information can be extracted, is the O 1s peak. Its position is relatively constant for all uranates, but it shows important variations in skewness. Previous studies have related the position and peak shape of the O 1s peak to the crystal structure (U–O bond lengths) [10]. A full discussion of the O 1s peak shape thus has to be postponed until the structure of the uranates is refined. This is currently being performed and will be published in a forthcoming paper [25].

5. Conclusion

The primary objective of our study was to investigate to what extent XPS can contribute to uranium valency determination in cesium uranates. Previous studies on similar systems had indicated that both position and satellite structure of the U 4f core level peaks are sensitive to the uranium valency, but the cesium uranate system was never included before. Our investigations have confirmed this sensitivity, but it has also been proven that the chemical shifts are minute and that some care must be taken when compensating for charging effects.

The series of cesium uranates included three compounds in which uranium has a valence state VI, and one phase ($Cs_2U_4O_{12}$) with multivalent uranium. On the basis of the U 4f peak and satellite analysis, it was shown that the uranium atoms are present as U^{VI} and U^{V}. The formula for the compound should therefore be written as $Cs_2(U_2^{VI}U_2^{V})O_{12}$.

It could be evidenced that the U 4f peak position not only depends on the valence state of uranium, but also on the Cs/U ratio. Within the series of cesium uranates with monovalent uranium (U^{VI}), the U 4f peak position varies by 0.4 eV when the Cs/U ratio goes from 0.5 to 1.

Valence band spectra clearly show the difference between pure U^{VI} compounds, where the U 5f line is absent since the U 5f shell is empty, and compounds with a lower uranium valency, which show the U 5f peak. Valence band analysis should be performed with care, since surface reduction can occur simply through exposure to the UHV in combination with the X-ray irradiation and it certainly occurs when the surface is sputtered. Whenever the surface is reduced, the satellite structure and U 4f peaks are modified too.

Regarding the future application of XPS for the determination of the uranium valency in nuclear irradiated fuel, both of the matrix and of the uranate phases formed, the prospects are ambiguous. On the one hand, it is clear that XPS is technically capable of providing important information, but on the other hand, experiments will be complicated by the numerous factors that influence the spectrum details.

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