

A Study of Synthetic and Natural Uranium Oxides by X-ray Photoelectron Spectroscopy

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Abstract. Synthetic and natural uranium oxides UO_x ($2 \leq x \leq 3$) have been studied with *X-ray photoelectron spectroscopy* (XPS) to determine the phase composition and content of uranium ions in uraninites with a varying degree of oxidation. A strong hybridization of U_{6p} and O_{2s} orbitals has been found which permits a quantitative assessment of the U–O bond lengths. The values of such bonds in some substances have been found to be smaller than those in synthetic U(VI) oxide. The oxides U_2O_5 and U_3O_8 contain two types of uranium ions with a varying degree of oxidation.

Introduction

A knowledge of the relationships between uranium ions with different degrees of oxidation that are found in uraninites and of the phase composition of these oxides is essential to any study of their formation conditions on which exploration is to be based. These problems have so far remained unresolved (Dymkov 1973). Chemical methods of determining the relationships between the different uranium ions in an oxide are based on solution of a sample in strong acids and thus inevitably open to error. As far as physical methods are concerned, the most effective approach to such studies is to use X-ray structure and microdiffraction techniques; however, these methods can only find limited applications when amorphous subjects have to be studied.

The purpose of the present paper is to see if it is possible to solve this problem by *X-ray photoelectron spectroscopy* (XPS).

Experimental

X-ray photoelectron spectra were obtained on a Hewlett-Packard (HP 5950A) electrostatic spectrometer using monochromatic $AlK_{\alpha 1,2}$ (1486.6 eV) X-ray radiation at a vacuum of 1.10^{-9} torr and room temperature. The spectrometer resolution measured with respect to a *full linewidth at half maximum* (FWHM) of the $Au_{4f(7/2)}$ electrons is 0.8 eV. The binding energies (E_b) in our paper are given with respect to that of the C_{1s} electrons of diffusion oil, taken as 285.0 eV. We have observed the $Au_{4f(7/2)}$ line at $E_b = 83.8$ eV, and the C_{1s} line of diffusion oil on a gold substrate – at $E_b = 284.4$ eV.

The samples prepared for study were in the form of finely dispersed powders of the synthetic and natural oxides deposited

from tetrachlormethane (CCl_4) and cyclohexane (C_6H_{12}) on to a titanium substrate. Compacted layers of the same powders were also pressed into a indium substrate. In addition, uraninite samples were prepared as polished plates of the mineral. The uraninite spectra gave practically no evidence for the existence of possible impurities (within the sensitivity range of the method used), except for the O_{1s} and O_{2s} lines. A low-energy electron gun was used to remove a photoelectron-induced charge accumulated on the sample during spectrum measurements. For each sample the spectra were taken at least 3 times. The data thus obtained for the samples prepared by the different techniques were the same within the limits of experimental error.

The separation of the lines into individual components, determination of the electron binding energy, XPS line areas and FWHM were effected by an HP 2100 A computer using an algorithm from Mikhailenko et al. (1973). The precision of the electron binding energy was within 0.2 eV, and the line intensities – about 10%.

When line separation in the spectra could not be accomplished because of a heavy overlap, the binding energies of the uranium oxide valence and inner electron levels were obtained as a weighted average of the binding energy of the electrons belonging to the ions of different degrees of oxidation.

Uranium oxides were prepared by the standard methods: U_3O_8 by the calcination of uranyl nitrate at 900° C; U_2O_5 by leaching U_3O_8 with sulphuric acid and subsequent heating of the residue in a helium current at 120° C; $UO_{2.06}$ by the reduction of U_3O_8 in hydrogen; γ - UO_3 by the calcination of uranium peroxide hydrate at 250 to 300° C (Katz and Rabinovitch 1951; Blinova et al. 1961). U_4O_9 was produced by the oxidation of UO_2 at 170° C in air, followed by prolonged calcination at 800° C in vacuo (Blinova et al. 1973). The oxide on the surface of a metal plate, designated UO_2 (M), was obtained by a method similar to that used by Evans (1977). Oxygen coefficients (x) for the natural oxides UO_x were determined by a chemical method (Lisitsin 1975). The samples of uraninite in the authors' collection were obtained from various mineralogical museums in the USSR without any indication of locality.

Results

This paper presents XPS data relating to the valence and inner U_{6p} , U_{5d} , U_{5p} , U_{4f} , U_{4d} , O_{2s} , and O_{1s} electrons in the energy range 0 to 1 keV for a number of synthetic and natural oxides as well as for various finely-dispersed mixtures of the oxides,

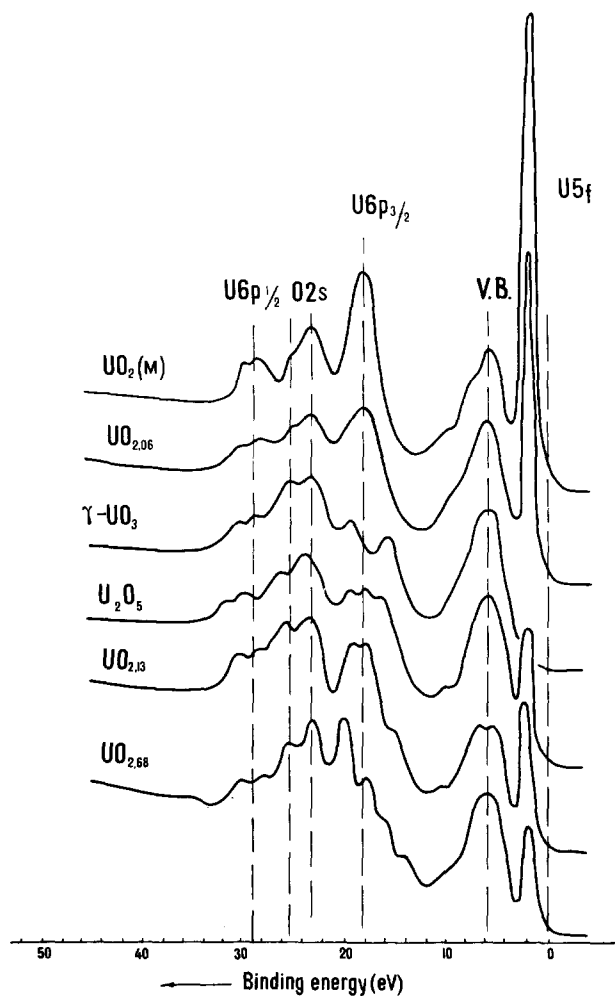


Fig. 1. XPS spectra of low-energy electrons for the synthetic oxides and uraninites ($\text{UO}_{2.13}$, $\text{UO}_{2.68}$)

$\text{UO}_{2.06}$ and γUO_3 obtained by grinding in an agate mortar in chromatographically pure heptane (C_7H_{16}). The results are presented in Figs. 1–6, in Table 1 as well as in the text of this paper. For ease of discussion, the authors use spectroscopic notation in the presentation of the spectral lines, both for the atomic and molecular orbitals. In so doing the degree of uranium oxidation in UO_2 and UO_3 is formally taken to be IV and VI, respectively.

For the complex oxides containing uranium ions of different degrees of oxidation, the binding energies of the U_{6p} ($3/2$) electrons ($E_b\text{U}_{6p(3/2)}$) of the U(VI) ion are listed in Table 1.

Lines were identified and spectra interpreted using data from previous studies. Thus it has been assumed, from neutron-diffraction data, that in U(IV) compounds the U_{5f} electrons not involved in the chemical bond are strongly localized at the central ion (Frazer et al. 1965). This assumption has been confirmed by XPS data (Fuggle et al. 1974; Verbist et al. 1974; Evans 1977) and theoretical calculations (Gubanov et al. 1977, 1979). Therefore for the uranium oxides whose degree of oxidation is less than (VI) the quantitative characteristics of the U_{5f} electrons not participating in the chemical bond can be obtained from (I), the intensity of their lines which is given here in relative units as the ratio between the intensities of the U_{5f} and U_{4f} ($7/2$) lines: $I = I_{\text{U}_{5f}}/I_{\text{U}_{4f}}(7/2)$. To minimize errors when determining (I), the spectra were scanned in turn by a special computer program in the 10 eV interval of the U_{5f} and U_{4f} ($7/2$) electrons

Table 1. Binding energies E_b (eV) and differences in the binding energies ΔE_b (eV) of the electrons, FWHM values δE_b (eV) and relative content (%) of uranium ions (k), in uranium oxides

No. of oxide	Oxide	$E_b\text{U}_{5f}$	VB	$E_b\text{U}_{6p(3/2)}$	$\sum^{\#}$	Π_u	$\Delta E_b\text{U}_{6p}$ ($3/2$) (A_1)	$E_b\text{U}_{6p}$ ($1/2$)	$E_b\text{O}_{2s}$	$\frac{\sum_g}{\sum_u}$	$\Delta E_b\text{O}_{2s}$ (A_2)	$E_b\text{O}_{1s}$	$\Delta E_b\text{O}_{1s}$	$E_b\text{U}_{4f}$ ($7/2$)	$\delta E_b\text{U}_{4f}$ ($7/2$)	k		
																U(IV)	U(V)	U(VI)
1	$\text{UO}_2(\text{m})$	1.9	6.1	18.0			28.6	23.2	530.6		2.2	380.8	1.8	68	26	6		
2	$\text{UO}_{2.06}$	1.9	6.1	18.0			28.5	23.3	530.5		2.2	380.9	2.1	65	29	6		
3	$\gamma\text{-UO}_3$	—	6.2	15.7		19.4	28.9	30.4	531.4		2.5	382.4	1.5	—	—	100		
4	$\gamma\text{-UO}_3 \cdot 2\text{H}_2\text{O}$	—	6.3	15.5		20.1	28.6	31.1	531.5		2.5	382.5	1.9	—	—	100		
5	U_4O_9	2.1	6.2	17.8		19.3	28.4	31.1	530.8		2.1	381.8	2.8	9	66	25		
6	U_2O_5	2.0	6.0	15.8		19.6	28.9	31.2	530.5		2.2	381.9	2.6	—	50	50		
7	U_3O_8	2.1	6.0	16.0		19.4	29.2	31.1	530.5		2.8	382.1	2.1	—	33	67		
8	$\text{UO}_{2.13}$	2.0	6.2	15.4		19.0	28.6	30.1	530.5		2.6	381.4	2.9	33	54	13		
9	$\text{UO}_{2.23}$	2.0	6.3	15.5		19.5	28.7	31.2	530.8		2.3	381.6	2.7	12	65	23		
10	$\text{UO}_{2.24}^a$	2.0	6.2	14.4		19.6	28.7	30.7	532.0		2.7	381.7	2.6	2	74	24		
11	$\text{UO}_{2.47}^a$	1.9	6.1	15.7		20.5	28.3	30.5	531.7		2.0	381.9	2.7	60	40	40		
12	$\text{UO}_{2.47}^b$	2.0	6.2	16.0		20.6	28.5	30.2	530.5		2.5	381.5	2.0	60	—	40		
13	$\text{UO}_{2.60}$	2.0	6.1	14.7		19.8	28.8	30.6	530.5		3.0	381.9	2.7	49	—	51		
14	$\text{UO}_{2.63}$	2.0	6.2	16.0		19.5	28.9	30.9	532.0		2.6	381.7	2.5	37	—	63		
15	$\text{UO}_{2.68}$	1.9	6.1	16.1		17.9	28.7	30.1	531.3		2.5	381.8	2.9	—	—	68		

E_b = Binding energy; VB = Valence band

^{a, b} Samples from different deposits;

^c Energies in the brackets correspond to the additional spectrum peaks

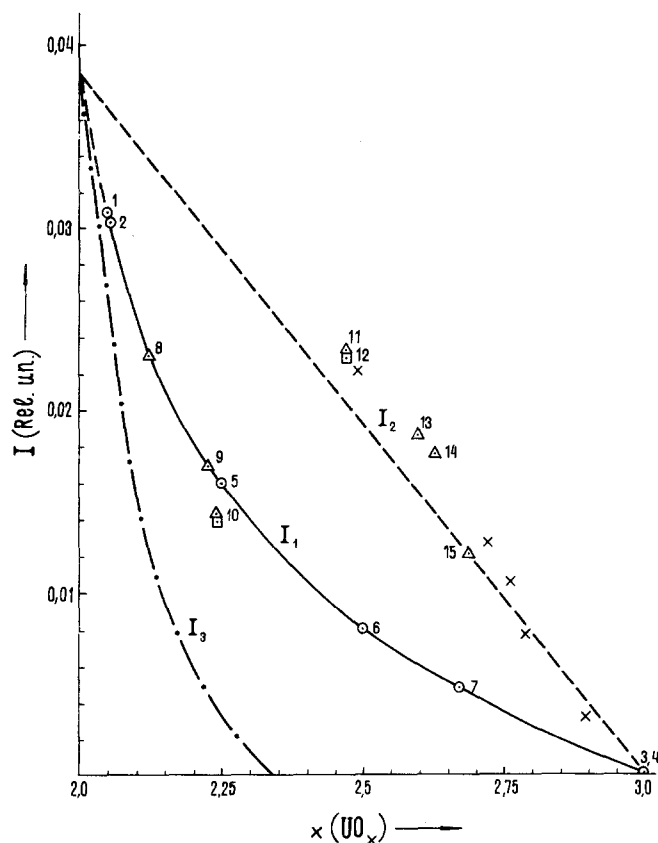


Fig. 2. Dependence of the relative XPS line intensity of U_{5f} electrons (I) on the oxygen coefficient (x) of uranium oxides UO_x : — I_1 (Eq. (1)); --- I_2 (Eq. (2)); - · - · - I_3 (Eq. (3)); \circ , synthetic oxides; Δ , \square —uraninites; \times , mixtures of UO_2 and γ - UO_3 (numbers correspond to the serial number of oxides in the table)

during spectrum production. Attempts to obtain an experimental value for the relative intensity of the U_{5f} electrons in UO_2 did not lead to positive results, although it has been postulated (Fuggle et al. 1974; Veal and Lam 1974; Verbist et al. 1974; Evans 1977) that the dioxide should form on the surface of a plate of uranium metal. Despite the fact that the spectrum shape and the ratios between the intensities of the different lines of the low-energy electrons of this oxide when formed by different oxidation methods are in good agreement with data reported in the literature (Fuggle et al. 1974; Veal et al. 1974; Verbist et al. 1974; Evans 1977) the relative intensity of the U_{5f} line in different runs was not significantly higher than that found for $UO_{2.06}$ (Fig. 2). For purposes of comparison, the spectra of the oxide formed on the surface of the uranium plate and designated $UO_2(M)$ are also given in the present work.

The percentages of UO_2 and UO_3 in artificial mixtures were determined from the intensity ratio of the U_{4f} lines which can be separated in the spectrum (Fig. 4).

Discussion

Synthetic Oxides

The Spectra of the U_{5f} Electrons. The intensity of the U_{5f} line decreases as the oxygen coefficient x ($2 \leq x \leq 3$) increases, and in the γ - UO_3 spectra this line can no longer be observed (Fig. 1). For the synthetic oxides the dependence of the U_{5f} line on the oxygen coefficient is nonlinear. In Fig. 2 the depen-

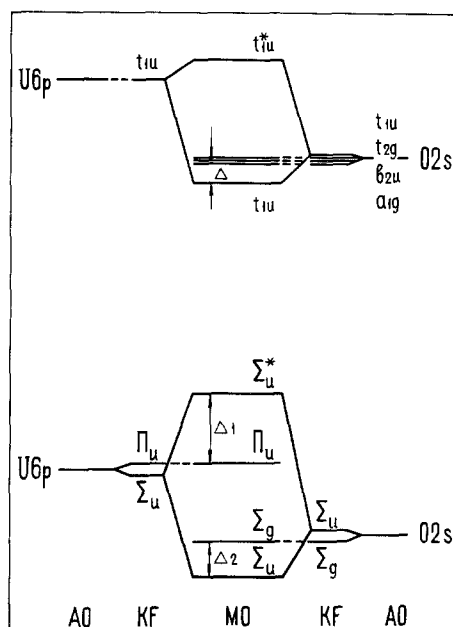


Fig. 3. Scheme of the molecular orbitals due to U_{6p} and O_{2s} atomic orbitals, for UO_2^{2+} clusters (symmetry group $D_{\infty h}$) and UO_3^{2-} clusters (symmetry group O_h)

dence represented by the solid curve was obtained by the least-squares method and has the form:

$$I_1 = 5.366x^{-7.173} \quad (1)$$

where I_1 is the relative intensity of the U_{5f} line, x is the oxygen coefficient for UO_x ($2 \leq x \leq 3$). This curve is in reasonable agreement with the dependence of the magnetic susceptibility on the oxygen coefficient in UO_x oxides (Arrott and Goldman 1957). Such agreement is not unexpected as the intensity of the U_{5f} line in the XPS spectra of the uranium oxides is proportional to the number of free $5f$ electrons and these are largely responsible for the magnetic properties of these compounds.

The relative intensity value of the U_{5f} line for UO_2 , found from the extrapolation of the curve corresponding to expression (1), gives, when $x \rightarrow 2$, the expected dependence of the relative intensity (I_2) of the U_{5f} line, on the oxygen coefficient for uranium dioxide-trioxide mixtures (Fig. 2). This dependence has the form:

$$I_2 = 0.0383x + 0.1149. \quad (2)$$

As this expression defines the contribution to the decrease in the relative intensity of the U_{5f} line of the UO_x oxides with respect to the U(VI) ions only, it was useful in evaluating the relative content (k) of these ions in our samples (see Table 1). The deviation of the experimental values of this intensity for the oxide mixtures from those expected should be attributed not only to the error in the determination of the intensity of the U_{5f} line in UO_2 when extrapolating curve I_1 , but also to errors arising during the determination of the oxygen coefficients for these mixtures.

The difference in the relative intensities, $\Delta I = I_2 - I_1$ (expressions 1 and 2 and Fig. 2) characterizes the decrease in the content of U(IV) ions in the UO_x oxides and the appearance of ions with a greater degree of oxidation. Assuming that, as x increases, the synthetic oxides contain uranium ions of the degrees of oxidation IV, V and VI with electronic configurations $5f^2$, $5f^1$, and

$5f^0$, respectively, it will be possible to find approximately how the relative intensity (I_3) due to the U(IV) ions decreases. This dependence is expressed by the relation (Fig. 2):

$$I_3 = I_2 - 2(I_2 - I_1) = 2I_1 - I_2. \quad (3)$$

With this approximation the dependencies shown in Fig. 2 permit estimation of the relative content of the different uranium ions in the oxides (see Table 1). It can for example, be concluded that U_2O_5 and U_3O_8 contain mainly U(V) and U(VI) ions in the ratios 1:1 and 1:2, respectively.

It follows from the data of Figs. 1 and 2 and the Table 1 that the synthetic oxides ($2 < x < 3$) are not a simple mixture of dioxide and trioxide. Thus the intensity of the U_{5f} line, can be used to make a quantitative evaluation of the relative content (k) of uranium ions of different degrees of oxidation in complex oxides (see Table).

The Spectra of the U_{6p} and O_{2s} Electrons. The electron state of uranium ions in the oxides are further characterized by the spectra of the U_{6p} and O_{2s} electrons, observed in the region from about 12 to 32 eV (Verbist et al. 1974; Veal et al. 1975; Veal et al. 1977). Instead of the expected summary spectrum due to the superposition of the doublet from the U_{6p} electrons with the value of the spin-orbit splitting $\Delta E_{SL} \approx 10.5$ eV and the O_{2s} line, this region shows a more complex structure for the uranium oxides (Fig. 1). Such a structure has its poorest expression in the dioxide spectrum. As distinct from the UO_2 spectrum, the γ - UO_3 spectrum is more complex in the region of the $U_{6p}(3/2)$ electrons. Two clearly defined components are observed for these electrons. The splitting of the $U_{6p}(3/2)$ line when passing from UO_2 to UO_3 is, according to Veal et al. (1975), associated with a change of symmetry in the immediate environment of the uranium ions. In UO_2 the uranium ion is surrounded by eight oxygen ions disposed symmetrically at the cube vertices, whereas in UO_3 , this symmetry is disturbed as the result of the presence of the almost linear uranyl ion, the length of the R_{U-O} bond being shortened in UO_2^{2+} and lengthened between the central uranium ion and the oxygen ions in the equatorial plane. This leads to the asymmetry of the electric field around the central uranium ion, to which is ascribed the splitting of the $U_{6p}(3/2)$ line. In fact a dependence of the splitting value for the $U_{6p}(3/2)$ line on the bond length R_{U-O} in the uranyl ion of various compounds has been found experimentally (Veal et al. 1975).

As can be seen from Fig. 1, the spectra of the O_{2s} electrons are characterized by a complex structure containing at least two peaks (see Table 1). It is known that for the oxides of various metals the shift of the line of the O_{2s} electrons does not exceed that of the O_{1s} electrons. However, Table 1 shows that in our uranium oxides, the difference in the binding energies of the O_{2s} electrons is greater than that of the O_{1s} electrons by about 1 eV. It has also been shown (Miyake et al. 1975) that the presence in uranium compounds of two types of nonequivalent oxygen atoms, located in the axial and equatorial positions, leads only to a broadening of the O_{1s} line in the spectrum. In this connection the two O_{2s} lines observed in the γ - UO_3 spectrum cannot be ascribed to two types of oxygen atoms in this oxide, as previously proposed (Veal et al. 1975).

A calculation made by the method of the self-consistent X_α scattered waves-field (SCF X_α SW) in the nonrelativistic approximation for the UO_2^{2+} , UO_2^{1+} , UO_3^{0-} and UO_3^{1-} clusters has indicated that the appearance of two lines in the spectrum of the $U_{6p}(3/2)$ electrons is due not to the splitting of the $U_{6p}(3/2)$ level in the crystal field, as previously suggested (Veal et al.

1975), but rather to a strong hybridization of the U_{6p} and O_{2s} electrons in UO_2^{2+} and UO_2^{1+} . Such a hybridization occurs to a lesser extent in UO_2 . The results of this calculation are in good qualitative agreement with the spectra of the U_{6p} and O_{2s} electrons for γ - UO_3 and UO_2 and also with the $^{235m}UO_3$ conversion spectra (Zhudov et al. 1980), that characterize the energy distribution of the electrons of the hybrid and quasi-atomic orbitals, and are also in agreement with the results of theoretical work (Ellis et al. 1975; Walch and Ellis 1976; Gubanov et al. 1977, 1979). Such orbitals are shown schematically in Fig. 3. The spin-orbital splitting of the U_{6p} level of the U(VI) ion results in the observed spectrum of the low-energy inner electrons in γ - UO_3 becoming correspondingly more complex (Fig. 1 and Table 1). It follows also from the calculation that the shorter length of the R_{U-O} bond in UO_2^{2+} leads to a higher A_1 value (Fig. 3) which is consistent with earlier results (Veal et al. 1975; Walch and Ellis 1976). It should also be noted that the intensity of the low-energy component of the $U_{6p}(3/2)$ and O_{2s} electrons (Σ_u^*) for UO_2^{2+} should be half that of the component due to the quasi-atomic orbital of the $U_{6p}(3/2)$ electrons (I_{lu}). In this case the position of the line (I_{lu}) in the spectrum is bound to be less dependent upon the length of the R_{U-O} bond in UO_2^{2+} than that of the low-energy component (Σ_u^*), (Fig. 3). This agrees with the data obtained by the present authors (Fig. 1 and Table 1).

It follows from the above data that the structure of the spectra of the U_{6p} and O_{2s} electrons reflects not only the symmetry of the environment of the uranium ions in the oxides and permits differentiation between UO_2 and UO_3 but equally makes it possible quantitatively to evaluate the length of the R_{U-O} bond in UO_2^{2+} . This is especially important in the case of amorphous uranium oxides for which X-ray structure analysis is of limited application.

The Spectra of the U_{4f} and O_{1s} Electrons. Due to the fact that the binding energies of the inner UO_2 and UO_3 electrons differ by about 1.5 eV (Fig. 4 and Table 1), the presence of different oxidation states of the uranium ions in the complex oxides or mixtures can be established from the spectra of these electrons. Moreover, if the states of the uranium ions are close to U(IV), U(V) and U(VI), the relative content of such ions can be found from the spectra of the inner electrons. It will be seen from Fig. 4 that for U_2O_5 , U_3O_8 and the mixture $UO_2:UO_3=1:9$ the $U_{4f}(7/2)$ line consists of two components. This is also the case for the O_{1s} line of these oxides. However, it is difficult to assess quantitatively the different oxidation states of the uranium ions and to find an oxygen coefficient in UO_x from the spectrum of the O_{1s} electrons, as the surface of the synthetic oxides may contain adsorbed oxygen-bearing molecules, and the uraninite samples may contain oxygen associated with any impurities. Nevertheless the spectra of the O_{1s} electrons can be useful in supplying indirect qualitative conclusions as to the electronic state of the uranium ions in the oxides (Fig. 4 and Table 1).

It follows from these data that U_2O_5 and U_3O_8 contain two types of uranium ions. However, these oxides are not a mixture of two simple oxides - UO_2 and UO_3 (Fig. 2), but represent complex stable phases whose lattice incorporates two different types of interconnected uranium and oxygen ions. If we assume, as before that these complex oxides contain U(V) and U(VI) ions, then, by resolving the U_{4f} lines into two components, it will be possible to make a quantitative assessment of the proportion of each ion in these oxides (Fig. 4). On such an assumption U_2O_5 and U_3O_8 contain U(V) and U(VI) ions

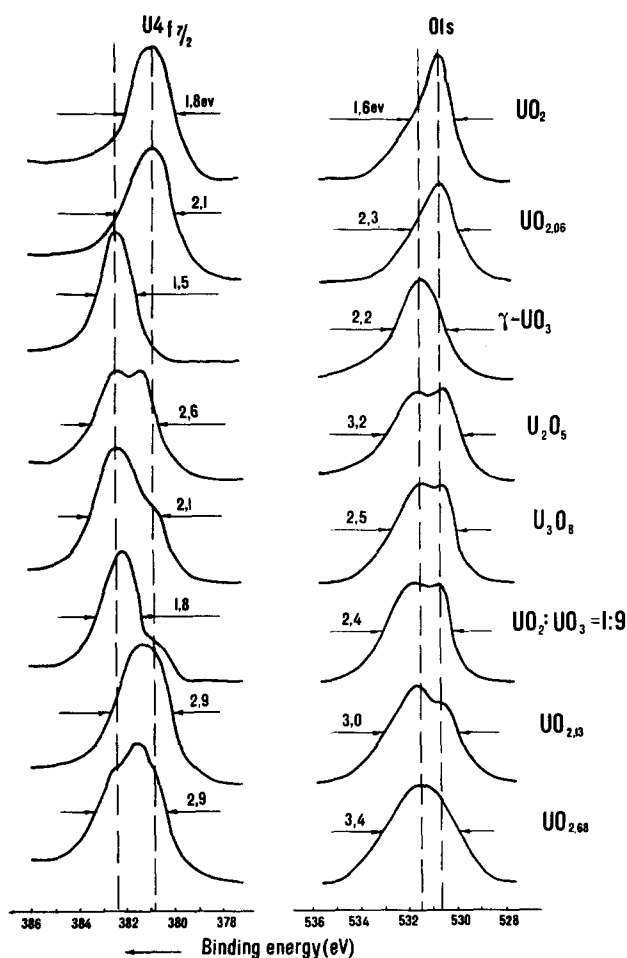


Fig. 4. XPS spectra of $U_{4f}(7/2)$ and O_{1s} electrons for synthetic uranium oxides and uraninites ($UO_{2.13}$ and $UO_{2.68}$). The intensities of different lines are not normalized to the same scale

in the ratios 1:1 and 1:2, respectively, which is consistent with the spectra of the U_{5f} electrons for these oxides. This is also confirmed by the relation between the intensities of the components of the $U_{4f}(7/2)$ lines and by the corresponding binding energies for the $U_{4f}(7/2)$ electrons, found by resolving these lines (U_2O_5 —381.5 and 382.3 eV; U_3O_8 —381.5 and 382.4 eV). As far as the relative content of the two types of uranium ions in these oxides is concerned, these data agree with previous results (Verbist et al. 1974; Thibant et al. 1977).

Despite the complex nature of the spectra of the $U_{6p}(3/2)$ electrons in U_2O_5 and U_3O_8 , peaks due to U(VI) ions can be distinguished in them. Two other components at 14.4 and 18.0 eV for U_2O_5 can probably be ascribed to U(V) ions (Fig. 1 and Table 1). The spectra of the O_{1s} electrons in these oxides consist of two components which correspond to the two oxidation states of uranium and possibly to adsorbed oxygen (Fig. 4 and Table 1).

Another characteristic of the electronic state of the uranium ion is the spectrum of the U_{4f} electrons, where one can observe shake-up satellites on the side of the higher binding energies with respect to the fundamental doublet lines (Fig. 5), (Veal et al. 1977; Weber et al. 1979). The distance from the fundamental line to the satellites (ΔE_{sat}) characterizes the chemical bond and it is not the same for different oxides. In the spectrum of the U_{4f} electrons in $UO_2(M)$ the satellites are spaced from the fundamental lines by about 7 eV, whereas the spectrum of

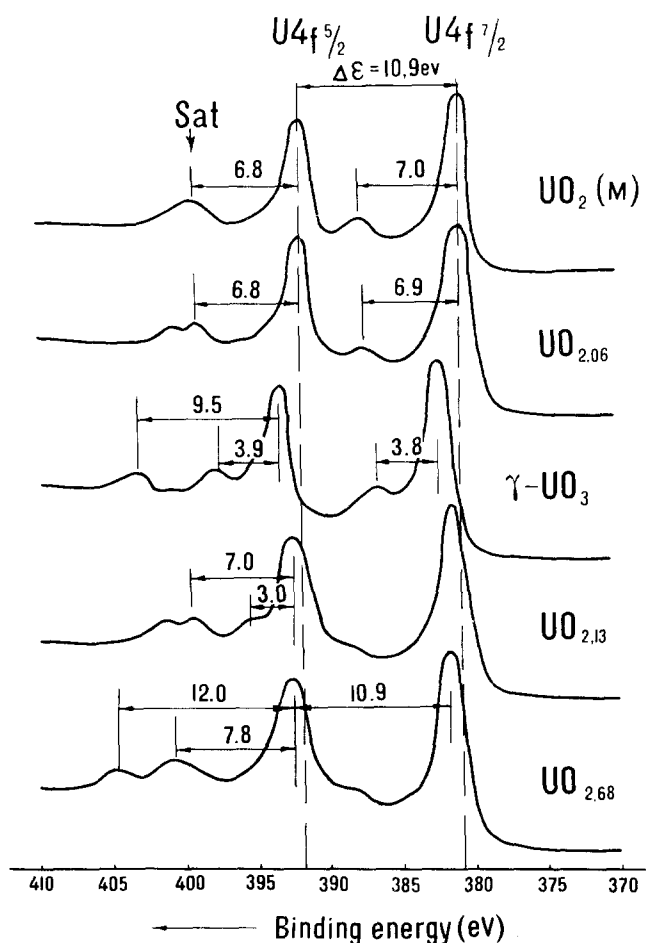


Fig. 5. XPS spectra of the U_{4f} electrons for synthetic uranium oxides and uraninites ($UO_{2.13}$ and $UO_{2.68}$)

these electrons in γ - UO_3 contains two satellites spaced from the fundamental lines by about 3.9 and 9.5 eV, respectively. In the spectra of the other oxides the satellites have a complex structure which in some cases can be compared with that of the simple oxides.

It should be noted that the intensity and structure of such satellites, along with the intensity of the U_{5f} lines, show a sharp change for a small increase in the oxygen coefficient x (at $x \geq 2$). (Figs. 1, 2, 5 and Table 1). This suggests that the excess oxygen introduced into the face-centred cubic lattice of UO_2 leads to a noticeable change in the degree of oxidation of some of the uranium ions and rearrangement of the chemical bond in UO_2 . This is due to the excess oxygen forming a chemical bond with uranium ions that have chemically active U_{5f} electrons (Veal and Lam 1974).

The Spectra of the U_{5p} , U_{5d} and U_{4d} Electrons. A more complex spectrum structure of the U_{5p} electrons in UO_2 and UO_3 and a relatively small signal-to-background ratio are responsible for difficulties in observing a doublet component of the $U_{5p}(3/2)$ electrons (Veal et al. 1975; Novakov and Hollander 1968). In the spectra of the $U_{5p}(3/2)$ electrons in these oxides one can observe not a doublet, as reported (Veal et al. 1975; Novakov and Hollander 1968), but a more complex structure (Fig. 6). In contradistinction to the data of Novakov and Hollander (1968), it has been found that on passing from UO_2 to UO_3 the separa-

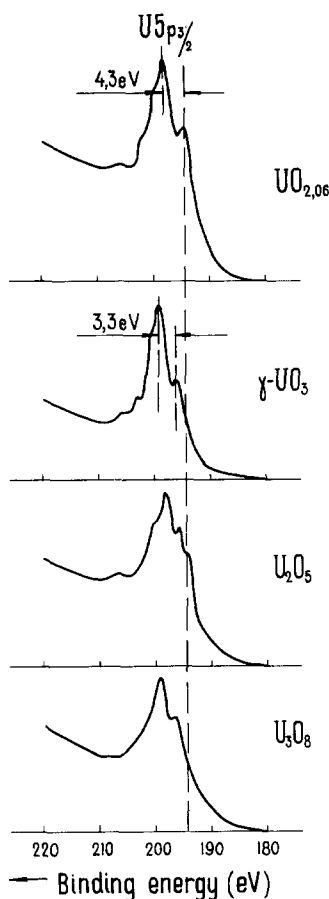


Fig. 6. XPS spectra of the $U_{5p}(3/2)$ electrons for synthetic oxides

tion value between the two clearly defined $U_{5p}(3/2)$ components of the spectrum decreases from 4.3 to 3.3 eV. These results are in good agreement with those of Veal et al. (1975). It should be pointed out that no mechanism explaining the appearance of the complex structure of the U_{5p} spectra has yet been established. However such a structure cannot evidently be due to the splitting of the levels in the crystal field (Veal et al. 1975). Despite this, the structure of the $U_{5p}(3/2)$ spectrum characterizes the oxidation state of the uranium ions. Since uranium ions can exist in different oxidation states in U_2O_5 and U_3O_8 , the total spectrum of the $U_{5p}(3/2)$ electron is observed as a superposition of the spectra characterizing these states (Fig. 6).

In the spectra of the U_{5d} electrons in the oxides studied there is a significant broadening of the $U_{5d}(3/2)$ line as compared with the $U_{5d}(5/2)$ doublet component. Thus the half-widths of the $U_{5d}(5/2)$ ($E_b=97.3$ eV) and $U_{5d}(3/2)$ ($E_b=105.6$ eV) components for $UO_{2.06}$ are 2.5 and 3.9 eV, respectively, whereas those of the $U_{5d}(5/2)$ ($E_b=98.4$ eV) and $U_{5d}(3/2)$ ($E_b=107.1$ eV) components for $\gamma-UO_3$ are 1.9 and 3.3 eV, respectively. It is assumed that such a difference in the relation between the half-widths of these doublet components for UO_2 is due to their multiplet splitting (Veal et al. 1977). However in the case of $\gamma-UO_3$ such a mechanism is not valid for the spectra of the U_{5d} electrons, as UO_3 contains no unbound U_{5f} electrons. On passing from UO_2 to $\gamma-UO_3$ our spectra show a line shift towards the higher binding energy region and a change in the spin-orbital splitting value (ΔE_{SL}). The decrease in the ΔE_{SL} value of the U_{5d} electrons for UO_2 by 0.4 eV as compared with that for $\gamma-UO_3$ may be due to the multiplet excitation in the UO_2 spectrum, as is seen in the $2p$ spectra of nickel compounds (Teterin et al. 1978).

In the U_{4d} spectra of the uranium oxides the doublet components have a relatively large half-width (about 5.5 eV), which impedes their separation into individual lines in the case of the complex oxides, but at a higher oxidation state of the uranium ions a shift of these lines towards the higher binding energies is observed.

Natural Oxides

Low-Energy Electron Spectra. The low-energy electron spectra for all the uraninite samples studied show a U_{5f} line and complex structure of the U_{6p} and O_{2s} spectra (Fig. 1 and Table 1). The spectra for the uraninites show the fine structure of the valence band and two clearly defined peaks in the O_{2s} spectrum, thereby manifesting a somewhat better resolution in these regions than do the synthetic oxide spectra. This is attributed to the fact that the synthetic oxides were prepared as layers of compacted powders, whereas the uraninites were in the form of mirror-polished plates.

As x changes from 2 to about 2.25, the dependence of the relative intensity of the U_{5f} line for the natural oxides, UO_x , is approximately the same as for the synthetic oxides. With further increase in x , there is a drop in the $5f$ line intensity, this decrease obeying the same law that characterises the change of intensity with x for mixtures of UO_2 and UO_3 (Fig. 2).

The complexity of the uraninite spectra for the U_{6p} and O_{2s} electrons is due to the superposition of the lines relating to uranium ions with different degrees of oxidation (Fig. 1 and Table 1). These spectra can be conveniently discussed in terms of molecular orbitals (Fig. 3). The interpretation will be simplest in the spectrum region of the U_{6p} electrons from about 12 to 22 eV, where an individual line due to the U(IV) ions or one of the U(V) lines observed at about 18 eV is superposed on to the $U_{6p}(3/2)$ and O_{2s} spectrum in UO_2^{2+} , composed of the two lines (Σ_u^* and Π_u). It will be seen from the spectra of these electrons for $UO_{2.13}$ and $UO_{2.68}$ that the intensities of the Σ_u^* components are lower than those of the Π_u components (Fig. 1). This is consistent with the results presented in Fig. 3. The appearance of two peaks, at 14.0 and 16.1 eV in the $UO_{2.68}$ spectrum in the region of the Σ_u^* electrons, is probably due to two types of ions being present in the sample. By using the experimental dependence of Δ_1 , on the length of the R_{U-O} bond in the uranyl ion (Veal et al. 1975), a quantitative assessment can be made of this bond length in the uranyl ion present in our uraninites.

Thus for $UO_{2.13}$ $R_{U-O} \approx 1.76$ Å, and for $UO_{2.68}$ $R_{U-O} \approx 1.73$ Å. If the phase due to the U(VI) ions were present in the samples in the amorphous state, it would be difficult to obtain this information from X-ray structure data.

Note that in the spectra of some uraninites the Δ_1 values for UO_2^{2+} listed in the Table 1, in a number of instances exceed the corresponding values for the synthetic oxides.

Two clearly defined peaks are seen in the region roughly between 22 and 27 eV on the U_{6p} and O_{2s} spectra for uraninite (Fig. 1 and Table 1). According to the energy scheme (Fig. 3) these peaks, in particular, correspond to the electrons of the molecular orbitals Σ_g and Σ_u of UO_2^{2+} as well as to the electrons of UO_2 . The different intensity of these lines can be explained both by the spectrum superposition of the lines of the UO_2 and UO_3 electrons and the O_{2s} line of the oxygen adsorbed on the sample surface. In this case, as for the synthetic oxides, the difference in the binding energy of the electrons responsible for these lines is far in excess of that of the O_{1s} electrons for the various uraninite samples (Figs. 1, 4 and Table 1). In those cases when the O_{1s} lines in the uraninite spectra cannot be sepa-

rated, their binding energies are given as the weighted average values of the binding energies for the the O_{1s} electrons of the various oxides. As already noted in the case of the synthetic oxides, it is difficult to determine the oxygen coefficient for uraninite from O_{1s} spectra.

In the $U_{6p}(1/2)$ spectra for various natural oxides, the region approximately between 27 and 32 eV shows a complex structure with two peaks (Fig. 1 and Table 1).

In the case of UO_2 a spectrum calculation with allowance made for the relativistic effects confirms the presence of two lines in this region (Gubanov et al. 1979).

It follows from the low-energy electron spectra that generally it is possible to isolate three ionic states in uraninite, approximating, the U(IV), U(V), and U(VI) degrees of oxidation, (see the Table 1).

The Spectra of the Inner Electrons. It is not possible to observe resolved individual components in the spectra of the $U_{4f}(7/2)$ electrons in the natural oxides. The spectrum of these electrons is seen as one broadened line with a weakly resolved structure (Fig. 4 and Table 1). The binding energies of the $U_{4f}(7/2)$ electrons, measured as a weighted average of the different ionic states, increases with the content of the U(VI) ions in the uraninites, as is to be expected with increasing concentration in the samples of uranium ions with a higher degree of oxidation. The fact that the spectra contain one common broadened line for the U_{4f} electrons indicates that uraninite does incorporate uranium ions of different degrees of oxidation.

The structure of the shake-up satellites in the U_{4f} electrons undergoes a substantial change when passing from the synthetic to the natural oxides (uraninites (Fig. 5). This is associated with a change in the nature of the uranium-oxygen chemical bond in the uraninites as compared with that in (synthetic) UO_2 and UO_3 . In particular, the increase in the energy of the separation of some satellite lines with respect to the main line points to an increasing difference in the energy of the molecular orbitals between which a charge transfer of type $O_{2s} \rightarrow U_{5f}$ occurs during the shake-up process. Such an increase in this difference can be due, for example, to a change in the length of the R_{U-O} bond and in the symmetry of the uranium ion environment in the uraninite as compared with those in synthetic UO_2 and UO_3 . Note that in the U_{4f} spectra for uraninites, except for the approximate coincidence of the positions of some satellite lines, no structure of the shake-up satellites, similar to that in the U_2O_5 and U_3O_8 spectra, is observed.

The doublet lines in U_{5d} spectra for uraninites, as in the spectra for the synthetic oxides, have different halfwidths which are a little greater than the halfwidths for the synthetic oxides. Such a line broadening is also evident in the spectra of the uraninite U_{4d} electrons. The binding energies of the U_{5d} and U_{4d} electrons, measured as weighted averages of different ionic states in the uraninites, increase, as in the case of the U_{4f} electrons, within a range of approximately 1 eV with increasing content of the U(VI) ion in the samples.

The $U_{5p}(3/2)$ spectra for uraninites show a complex structure that differs in shape from the spectra of all the synthetic oxides we have studied.

Conclusion

The data on the electronic structure of various uranium oxides, obtained by X-ray photoelectron spectrometry and discussed in this paper, show that this method could be extremely effective in studies of the natural oxygen-containing uranium compounds.

The method has been used to investigate a number of synthetic and natural oxides of uranium, in the case of the natural oxides, or uraninites being the first attempt to do so.

It is shown that the XPS method enables one to assess quantitatively the relative content of uranium ions of different degrees of oxidation in uraninites. It has been found experimentally and confirmed theoretically that there exists a strong hybridization of the U_{6p} and O_{2s} orbitals in the uranium oxides, which makes possible an evaluation of the bond length in uranyl ions, UO_2^{2+} , incorporated in the natural samples. In some instances the lengths of the R_{U-O} bond in the uraninites are shown to be shorter than those in the synthetic oxides. It is recognized that X-ray structure analysis is of limited value for the purpose of acquiring such information. The oxides U_2O_5 and U_3O_8 have proved to be a simple mixture of UO_2 and UO_3 but complex phases containing two types of uranium ions with degrees of oxidation close to U(V) and U(VI) present in the ratios 1:1 and 1:2, respectively. The uraninites are likewise complex phases.

When the oxygen coefficient x increases to $x \approx 2.5$, local regions are likely to appear in the uraninites; containing uranium ions whose degrees of oxidation are close to U(IV) and U(VI) with the result that the samples exhibit some properties of mixtures of UO_2 and UO_3 . It should be noted, however, that information obtained from the uraninite spectra (at $x > 2.47$) does not exclude the existence in these oxides of uranium ions whose degree of oxidation is close to V.

On passing from UO_2 to UO_3 the excess oxygen introduced into the UO_2 lattice forms a chemical bond with U(IV) ions containing chemically active free U_{5f} electrons. Especially intensive rearrangement of the chemical bond occurs at small increases of the oxygen coefficient ($x < 2.25$) in UO_x as compared with those in UO_2 .

The results obtained, taken as a whole, suggest that with respect to spectral characteristics the natural oxides differ from synthetic and are not simple mixtures of uranium dioxide and trioxide.

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