X-Ray Photoelectron Spectroscopy of Some Uranium Oxide Phases

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X-Ray photoelectron spectra of a variety of uranium oxides have been studied and compared with the spectrum obtained from the pure metal. The oxide phases studied were $UO_{2\cdot0}$, $UO_{2\cdot1}$, $UO_{2\cdot2}$, U_4O_9, U_3O_7, U_3O_8, and γ-UO_3 where the formal oxidation number of uranium alters from IV to VI. Significant chemical shifts observed for U 4*f* and O 1*s* peaks are explained by consideration of chemical structure and changes in uranium and oxygen oxidation states. The surface oxidation of uranium dioxide powder in air has been studied by comparing the spectra with those of UO_2 pellets and higher uranium oxides.

A STUDY of the oxidation state of uranium in irradiated nuclear fuel would be a valuable aid towards elucidation of the chemistry of nuclear fuel systems. In principle *X*-ray photoelectron (p.e.) spectroscopy[1,2] should be capable of distinguishing between different oxidation states. However such complicated systems can only be understood when sufficient data have been acquired from well characterised uranium compounds and for this reason an *X*-ray/p.e. study of uranium oxide systems was undertaken.

Initial studies[3,4] showed that there were significant chemical shifts between uranium 4*f* binding energies in the pure metal and those measured for the oxides UO_2, U_3O_8, and UO_3, the binding energies increasing with the formal oxidation state of uranium, from the metal to UO_3. Chemical shifts have also been detected in uranium Auger transitions.[5,6] However, the uranium–oxygen system is known to be complex. For example, a continuous range of stoicheiometries is available between UO_2 and U_4O_9 and metastable oxides such as U_3O_7 are known. Earlier reports revealed a degree of uncertainty over the precise value for the binding energy of $UO_{2\cdot0}$, which could have been caused by inhomogeneity of the previous samples, and therefore we report here an investigation into surface oxidation

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[1] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. J. Lindberg, ' ESCA—Atomic, Molecular, and Solid-state Structure studied by means of Electron Spectroscopy,' Almqvist and Wiksell, Uppsala, 1967, also new edn., North Holland Publishing Co., Amsterdam, in the press.

[2] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Henden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and U. Baer, ' ESCA applied to Free Molecules,' North Holland Publishing Co., Amsterdam, 1969.

[3] G. C. Allen and P. M. Tucker, *J.C.S. Dalton*, 1973, 470.

[4] D. Chadwick and J. Graham, *Nature. Phys. Sci.*, 1972, **237**, 127.

[5] G. C. Allen and R. K. Wild, *Chem. Phys. Letters*, 1972, **15**, 279.

[6] G. C. Allen and R. K. Wild, *J.C.S. Dalton*, 1974, 493.

properties of UO_2. We also report a study of a series of uranium oxides in which the stoicheiometry was varied in the range UO_2 to UO_3 ($UO_{2\cdot0}$, $UO_{2\cdot05}$, $UO_{2\cdot1}$, $UO_{2\cdot2}$, U_4O_9, U_3O_7, U_3O_8, and UO_3) and the formal oxidation number of uranium varied from IV to VI.

EXPERIMENTAL

Uranium Oxide Preparation.—The nature of the uranium–oxygen system is now fairly well understood. A recent paper[7] outlines the problems involved in preparing samples of known stoicheiometries and only brief details of the sample preparation are given here.

Two methods of preparing the oxide UO_2 were used. Samples of pure UO_2 powder were prepared by reduction of commercial UO_2 using CO containing 10% CO_2, and the oxides $UO_{2\cdot1}$, $UO_{2\cdot2}$, U_4O_9, and U_3O_7 were prepared by annealing weighed samples of pure UO_2 with the required quantities of pure oxygen at the temperature determined by the phase diagram. The oxide U_3O_8 was prepared by annealing samples of UO_2 in excess of oxygen at 500 K. The stoicheiometry of each sample was checked before measurement by reduction in carbon monoxide[7] and *X*-ray powder patterns were determined in each case. Generally, samples of good purity were obtained and stored in a desiccator, the vacuum being broken by CO–CO_2 to prevent surface oxidation. The U_3O_7 pattern showed that the sample was not completely pure, but this is hardly surprising in view of the metastable nature of U_3O_7, and was not a serious limitation since our primary objective was to study the change in electron-binding energies across a series of compounds with gradually altering stoicheiometries in the range UO_2 to UO_3.

Binding-energy and peak width at half-height ($\Delta_{\frac{1}{2}}$) values (eV) for selected peaks in uranium oxides *

Peak Compound	U $4f_{7/2}$ ($\Delta_{\frac{1}{2}}$) (±0·3)	U $4f_{5/2}$ (±0·3)	U $4d_{5/2}$ (±0·4)	U$4d_{3/2}$ (±0·4)	O 1*s* † ($\Delta_{\frac{1}{2}}$) (±0·2)
U metal ‡	377·1 (2·7)	387·8	736·8	788·9	
$UO_{2\cdot001}$ pellet	380·0 (2·1)	390·8			
UO_2 (after heating and cooling *in vacuo*)	380·1 (2·1)	391·0			530·4 (1·8)
UO_2 (as prepared powder)	380·3 (2·8)	391·2	738·9	781·5	530·4 (530·6sh)
$UO_{2\cdot1}$	380·6 (2·9)	391·4	738·9	781·5	530·3 (2·0)
$UO_{2\cdot2}$	380·7 (3·2)	391·5	739·4	781·7	530·6 (3·0)
U_4O_9	380·8 (3·1)	391·6	739·3	781·8	530·2 (2·7)
U_3O_7	380·8 (2·9)	391·6	739·3	781·6	530·1 (2·3)
U_3O_8	381·1 (2·7)	391·9	739·8	782·0	530·1 (2·4)
γ-UO_3 §	381·9 (3·2)	392·6			528·9 (2·5)

* Recorded relative to the Au $4f_{7/2}$ peak at 84·0 eV. † Peak position referred to centre of major constituent of peak (see Figure 4). ‡ Peak originally recorded at 1 073 K relative to Pt $4f_{5/2}$.[3] This value has been corrected relative to the Au $4f_{7/2}$ peak used in this work. § Many experiments were carried out on the γ-UO_3 system. The preparation and characterisation of anhydrous γ-UO_3 was hampered by difficulties involved in removing all the water without causing deoxygenation of the sample. However, despite this complication, we consider this value to be representative of anhydrous γ-UO_3.

UO_2 Pellets were prepared from pressed discs of U_3O_8 powder by heating in a vacuum of *ca.* 10^{-4} N m^{-2} at 1 700 K for several hours. The O : U ratios were determined in a solid-state electrochemical cell similar to that described by Hampson[8] and were found to correspond to $UO_{2\cdot05}$. To obtain samples with different O : U ratios oxygen was passed into one of the pellets to produce $UO_{2\cdot10}$ and forced out of another to produce $UO_{2\cdot001}$ by passing a current through the cell. The maximum O : U ratio that could be obtained (2·10) was determined by oxygen loss from the sample into the surrounding vacuum at the temperature of titration (*ca.* 1 300 K). *X*-Ray diffractometer traces taken of sintered $UO_{2\cdot05}$ pellets were consistent with published data for $UO_{2\cdot05}$, though a barely detectable amount of the oxide U_4O_9 was also present. The latter was absent from the diffractometer trace of the $UO_{2\cdot001}$ pellet.

Commercial γ-UO_3 was supplied by Hopkins and Williams and was shown to contain an unspecified quantity of water. This oxide is known in a wide range of hydrated forms[9] and, since a variation in water content has been shown to have quite a pronounced effect on the shift of the U 4*f* and O 1*s* peaks of the UO_3 sample,[10] samples were dehydrated in the spectrometer by careful warming to 433 K and pumping for *ca.* 10 min at a pressure of 1×10^{-3} N m^{-2}. Considerable care was necessary to avoid deoxygenation of the sample and therefore a finely ground sample was placed on the variable-temperature probe and warmed until the O 1*s* peak at 535·7 eV due to water was no longer discernible. This peak was quite distinct from the O 1s peak observed in anhydrous uranium oxides. A similar check was carried out on the other compounds but these freshly prepared samples were found to be free from this contaminant.

X-Ray Photoelectron Spectroscopy Measurements.—Binding energies were measured using a Vacuum Generators ESCA2 *X*-ray photoelectron spectrometer with Al-K_α *X*-radiation (1486·6 eV). Samples with a particle size of <50 μm were pressed into a gold-plated mesh. Charging effects were found to be important only for UO_3 and were compensated for by depositing a thin layer of gold on the surface of the sample.[11] Binding energies were measured relative to the gold $4f_{7/2}$ line at 84·0 eV. Heating of the samples was carried out resistively and the temperature was measured using a thermocouple and Comark electronic thermometer. During heating the vacuum condition at the sample was *ca.* 10^{-5} N m^{-2}. A Dupont 310 curve resolver was used in surface oxidation studies.

RESULTS AND DISCUSSION

Values of the binding energies determined for the series of oxides are given in the Table. We report values for the uranium 4*f* and 4*d* spin–orbit doublets and the oxygen 1*s* peak in each case. The 4*f* doublet

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[7] J. A. Crofts and T. Swan, C.E.G.B. Report, 1971, RD/B/N 2170.

[8] P. J. Hmapson, C.E.G.B. Report, 1973, RD/L/R1843.

[9] J. J. Katz and E. Rabinowitch, ' The Chemistry of Uranium, the Element and its Binary and Related Compounds,' McGraw-Hill, New York, 1951.

[10] G. C. Allen and P. M. Tucker, unpublished work.

[11] D. J. Hnatowich, J. Hudis, M. L. Perlman, and R. C. Regaini, *J. Appl. Phys.*, 1971, **42**, 4883.

is the sharpest and most intense in the uranium spectrum and is therefore best for comparison purposes. Shifts in the binding energy of this doublet for the pure metal, $UO_{2\cdot0}$, and γ-UO_3 are illustrated in Figure 1, whilst for comparison the less-dramatic changes along the series UO_x ($x = 2\cdot00$, $2\cdot1$, $2\cdot2$, $2\cdot25$, $2\cdot33$, and $2\cdot67$) are illustrated in Figure 2.

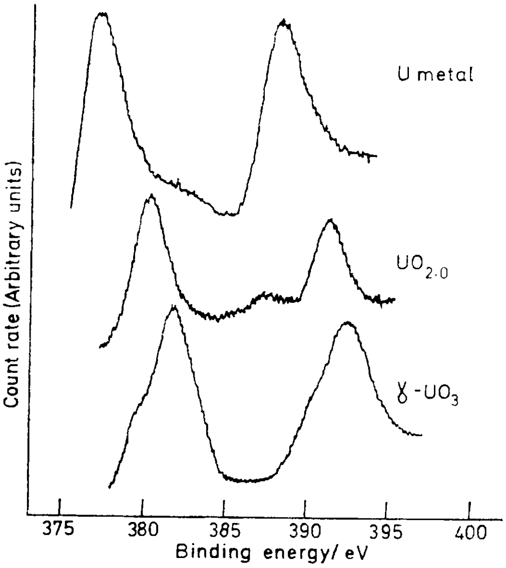

FIGURE 1 Effect of oxidation state on the binding energy of the uranium $4f_{7/2}$ and $4f_{5/2}$ doublet

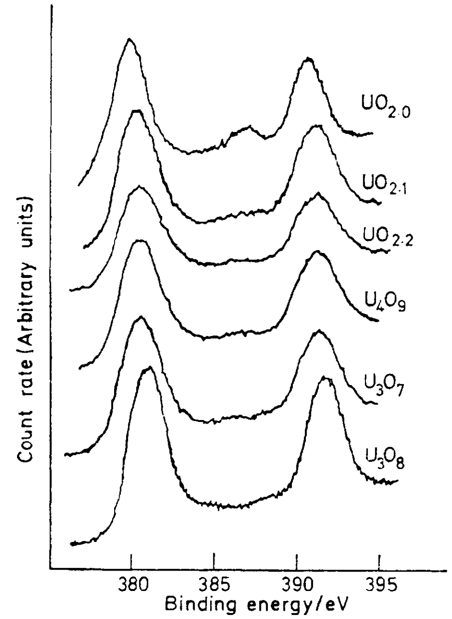

FIGURE 2 Effect of stoicheiometry changes on the binding energy of the uranium $4f_{7/2}$ and $4f_{5/2}$ doublet in the system UO_x ($x = 2\cdot0$, $2\cdot1$, $2\cdot25$, $2\cdot33$, and $2\cdot67$)

It is apparent from the Figures and by reference to the Table that the U $4f_{7/2}$ binding-energy shifts within this series follow a well defined path. Thus there is a large change (3·0 eV) in the *U* $4f_{7/2}$ peak binding energy when the metal and $UO_{2\cdot0}$ are compared. Thereafter a more gradual increase in binding energy was observed as the stoicheiometry of the essentially UO_2-type structure was altered through the series $UO_{2\cdot1}$, $UO_{2\cdot2}$, U_4O_9, to the tetragonal U_3O_7 and orthorhombic U_3O_8. The total shift in the $4f_{7/2}$ peak across this series amounts to only 1·0 eV, but a further shift of 0·8 eV is apparent when γ-UO_3 is compared with U_3O_8. The measured difference of 1·0 eV between $UO_{2\cdot0}$ and U_3O_8 was confirmed by recording the spectra of these oxides simultaneously and deconvoluting the resultant peak. For comparison, half-height peak widths ($\Delta_{\frac{1}{2}}$) are also given for the U $4f_{7/2}$ and O 1*s* peaks. $\Delta_{\frac{1}{2}}$ Values have been found to provide an indication of change in chemical structure, and are considered here to reflect the extent of disorder in the systems investigated.

The changes in binding energy and peak profiles are discussed below in terms of stiuctural variations, oxidation state of the uranium atom, and mixed-valence effects. Satellite peaks observed in the oxide spectra are considered in relation to optical band gaps.

Oxide Structures.—The structures of various uranium oxides have been reviewed by Cordfunke [12] and Eyring.[13] Willis [14] studied the structures of the oxides UO_2, $UO_{(2+x)}$, and U_4O_9 by neutron diffraction and a more recent assessment of the structure of U_4O_9 has been reported by Masaki and Doi.[15] The crystal structure of the oxide γ-UO_3 was originally reported in 1963 [16] and a recent paper [17] has substantiated the basic conclusions, whilst indicating that some of the earlier reported U–O bond distances were in error. The structures of the $UO_{(2+x)}$ phases are related to the fluorite structure of $UO_{2\cdot0}$, in which the co-ordination is 8 : 4. The structures of the phases $UO_{2\cdot1}$ and $UO_{2\cdot2}$ may be viewed as defect clusters formed by interstitial addition of oxygen rather than removal of uranium; the uranium sub-lattice is undisturbed by rearrangement of the atoms in the oxygen sub-lattice. The disorder increases from the phase $UO_{2\cdot1}$ to $UO_{2\cdot2}$ as more oxygen is added, but at room temperature the oxide is a mixture of $UO_{(2+x)}$ and $U_4O_{(9-y)}$, the latter having a structure similar to that of $UO_{(2+x)}$. Thus there is an increase in the average oxidation state, and consequent decrease in ionic size, leading to a decrease in the lattice constants.

These changes are reflected in the position and width of the uranium 4*f* and oxygen 1*s* peaks in the spectrum (see Figure 2 and Table). Thus, comparing the phases $UO_{2\cdot1}$ and $UO_{2\cdot2}$ with stoicheiometric $UO_{2\cdot0}$, the U $4f_{7/2}$ peak shifts to higher binding energy as the oxidation state is increased. The incorporation of interstitial oxygen and progressive disordering of the lattice is also reflected in increasing $\Delta_{\frac{1}{2}}$ values for the

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[12] E. H. P. Cordfunke, 'The Chemistry of Uranium,' Elsevier, Amsterdam, 1969.

[13] L. Eyring, 'Refractory Oxides of the Lanthanide and Actinide Elements,' in 'High Temperature Oxides Part II,' Academic Press, New York, 1970.

[14] B. T. M. Willis, *J. Phys. Rad.*, 1964, **25**, 431.

[15] N. Masaki and K. Doi, *Acta Cryst.*, 1972, **B28**, 785.

[16] R. Engmann and P. M. de Wolff, *Acta Cryst.*, 1963, **16**, 993.

[17] S. Siegel and H. R. Hoekstra, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 455.

O 1*s* and U $4f_{7/2}$ peaks. Naturally the effect is more pronounced for the O 1*s* peak in view of the different types of oxygen atom present in these oxides. At the composition $UO_{2\cdot25}$ the oxygen atoms become ordered over a long range to form the new phase U_4O_9. The basic fluorite lattice is maintained but the interstitial oxygen ions now form a structure which extends in each direction over four of the basic fluorite cells. There is one predominant uranium and oxygen environment in this compound, although a small proportion of both cations and anions are displaced from regular fluorite positions.[15] The observed *X*-ray photoelectron spectrum showed a slight sharpening of the U 4*f* and O 1*s* peaks relative to that of $UO_{2\cdot2}$, which may be due to the more regular structure.

In the phases U_3O_7 and U_3O_8 still more oxygen is incorporated in to the uranium lattice resulting in further degradation of the fluorite structure. Indeed U_3O_7 exists in a metastable tetragonal phase (tending to become a binary mixture of U_4O_9 and U_3O_8), whilst U_3O_8 is most commonly found at room temperature in the α phase which has a cubic face-centred orthorhombic unit cell. Both the phases U_3O_7 and U_3O_8 exhibited U 4*f* and O 1*s* peak positions that followed the trends previously established; that is, increasing addition of oxygen to the lattice causes a gradual increase in uranium binding energies. In both cases, however, the peak profiles were marginally sharper than in U_4O_9, but the basic fluorite structure that existed in the range UO_2 to $UO_{2\cdot25}$ no longer remains in these phases and thus a comparison is probably not reasonable. Nevertheless in both cases the $\Delta_{\frac{1}{2}}$ values were in excess of those found for the $UO_{2\cdot0}$ phase, in line with the observation that the structures are more complicated. Certainly in the case of the phase U_3O_8 two distinct uranium environments can be observed in the crystal structure [18] and this has been interpreted in terms of a mixed-valence structure.[18,19]

The structure of the phase γ-UO_3 is a complicated one which may be considered as two distorted octahedral arrays, each with its own primary and secondary bonds.[17] Basic differences between this and the $UO_{(2+x)}$ phases are the drop in co-ordination number of uranium from eight in the fluorite structures to six in this structure, and the decrease in average U–O bond lengths. The particularly short bonds of less than 2×10^{-10} m have been described as uranyl bonds and the structure has been formulated as uranyl uranate $[UO_2]UO_4$. However, despite this conjecture, the structure determination shows that the uranium atoms are both in a composite environment which is again reflected in peak widths of the U 4*f* doublet and the O 1*s* peaks. The spectrum of the anhydrous form of this material was difficult to obtain (see above) and the broadening of the O 1*s* peak to high binding energy may be a spurious effect. Such broadening would be expected if the formulation $[U^{VI}O_2]^{2+}(U^{VI}O_4)^{2-}$ is correct, although it is possible that uneven charging of the sample surface may be responsible for broadening effects.

Oxidation-state Changes and Mixed-valence Effects.—The oxidation state of uranium in these compounds may be formally described as a transition from zero in the metal to IV in the compound $UO_{2\cdot0}$ and VI in the case of γ-UO_3. This is reflected in the position of the $4f_{7/2}$ peak in the spectrum in each case. Compared to the metal the peak occurs at +3·0 eV in UO_2, and at +4·8 eV in γ-UO_3.

If a linear relation is assumed to exist between oxidation number and binding energy, the changes in the measured uranium 4*f* binding energy are, at first sight, not difficult to explain. A change of 0 to IV in the formal oxidation number produces an increase of 3·0 eV in binding energy, whilst a further change from IV to VI produces the additional increase of 1·8 eV. However, as has already been explained, other factors are involved, most notably a change in the uranium–oxygen co-ordination number, and correspondingly a change in structure and bond lengths, all of which contribute to the potential experienced by the uranium atom and which therefore affect the kinetic energy of the ejected electrons. Interestingly, the general trend of the O 1*s* peak to move to lower binding energy across the $UO_{(2+x)}$ series is reversed in the case of the oxide UO_3. The increase in binding energy of oxygen in the latter is probably a consequence of the greater polarising ability of U^{VI}. Addition of further oxide ions to those initially present in the fluorite lattice in the $UO_{(2+x)}$ series, although leading to a tendency for the uranium oxidation state to increase,[20] also provides a means whereby each oxygen ion loses less of its electron density to the uranium ions thus marginally decreasing oxygen binding energies.

The oxides U_4O_9, U_3O_8, and U_3O_7 are considered to be mixed-valence compounds.[18,21] While it must be acknowledged that Madelung-potential effects could considerably affect arguments about peak positions in terms of oxidation states, nevertheless the U $4f_{7/2}$ peak showed no clear evidence to indicate that it could be composed of overlapping peaks in these systems.

Surface Oxidation of UO_2.—It has been noted that uncertainty over the correct UO_2 binding energies probably results from the difficulty in obtaining homogeneous samples because of surface oxidation. This problem has been investigated further. Surface oxidation of the oxide UO_2 is known to occur in air even at room temperature.[12] A U_3O_7 phase is generally thought to be formed when UO_2 is oxidised below 400 K, though very small UO_2 particles (100 Å) are oxidised to UO_3 in air at room temperature. The starting point for the experiments was $UO_{2\cdot001}$ in fused pellet form, the spectrum of which is shown in Figure 3(*a*). On heating the $UO_{2\cdot001}$ pellets to 800 K in the spectrometer under

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[18] B. O. Loopstra, *Acta Cryst.*, 1964, **17**, 651.

[19] M. R. Robin and P. Day, 'Mixed Valence Chemistry,' *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[20] J. S. Anderson, D. N. Edgington, L. E. J. Roberts, and E. J. Wait, *J. Chem. Soc.*, 1954, 3324.

[21] K. Gotoo, S. Nomura, and K. Naito, *J. Phys. Chem. Solids*, 1965, **26**, 1679.

high vacuum, no changes either in binding energies or spectrum appearance were observed at 800 K or on subsequent cooling to room temperature under vacuum.

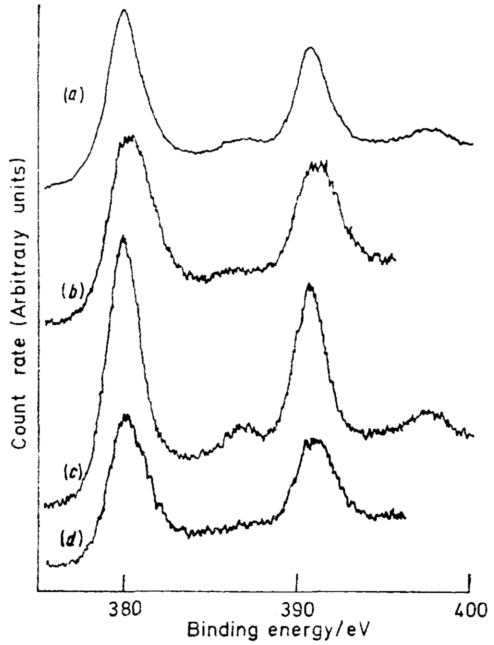

FIGURE 3 *X*-Ray photoelectron spectra showing uranium $4f_{7/2}$ and $4f_{5/2}$ lines obtained from the phase $UO_{2\cdot001}$: (*a*) pellet at room temperature; (*b*) powdered pellet at room temperature; (*c*) powdered pellet at 800 K; and (*d*) powdered pellet after cooling and exposure to air

This suggests that the spectrum in Figures 1 and 3(*a*) is indeed that of ' pure ' UO_2 and that the fused pellets are stable in air. However, UO_2 prepared by gaseous reduction of the commercial oxide did show a slight shift in uranium peak binding energy when heated and then cooled under the same conditions within the spectrometer.

The spectrum of the powdered sample of $UO_{2\cdot001}$, obtained immediately after the pellet had been ground in air, is shown in Figure 3(*b*). Three features of the new spectrum are apparent. First, the photoelectron peaks are considerably broader; secondly, the peaks are at higher binding energies by *ca.* 0·3 eV than those in Figure 3(*a*); and, finally, the satellites, which are conspicuous in the spectrum of the $UO_{2\cdot001}$ pellet, are no longer observed. The peak widths were not reduced by pumping for long periods. Heating of the powdered specimen at *ca.* 800 K under vacuum in the spectrometer resulted in the spectrum shown in Figure 3(*c*), which is similar in apearance to that of the $UO_{2\cdot001}$ pellet [Figure 3(*a*)], and the measured binding energies and half-widths for the peaks are the same. In fact, it is possible, using a curve resolver, to show that the peak shapes in the spectra in Figures 3(*a*) and (*c*) are identical. Prolonged heating at 800 K under vacuum did not result in any further change in the spectrum, nor did cooling to room temperature. However, subsequent exposure of the sample to air at atmospheric pressure at room temperature again resulted in broadening of the peaks with a corresponding slight shift to higher binding energy [Figure 3(*d*)]. This effect could be reversed by further heating of the sample at 800 K under vacuum.

Length of exposure to air was found to be important. Powder from the crushed $UO_{2\cdot001}$ pellet was left exposed to air for several days. Subsequently, the uranium $4f$ peaks showed a greater broadening effect and, therefore, a larger chemical shift than was the case for the sample studied immediately after the $UO_{2\cdot001}$ pellet had been crushed. The relevant $4f_{7/2}$ peaks are shown in Figure 4 (*b*-1) and (*c*-1). The spectrum of the old powdered specimen reverted to that of the $UO_{2\cdot001}$ pellet [Figure 3(*a*)] at *ca.* 800 K. Similar results were obtained with the $UO_{2\cdot05}$ samples. The binding energies of the $UO_{2\cdot05}$ pellets were the same within experimental error as those of $UO_{2\cdot001}$. Exposure to air for several days of $UO_{2\cdot10}$ powder formed from the crushed $UO_{2\cdot10}$ pellet resulted in an increase of 0·5 eV in $\Delta_{\frac{1}{2}}$. Heating this powder sample gave rise to a spectrum identical to the $UO_{2\cdot001}$ rather than the $UO_{2\cdot10}$ pellet, from which it must be concluded that the samples lose oxygen from the surface to the vacuum. In general, the shifts and peak-broadening effects produced by grinding of

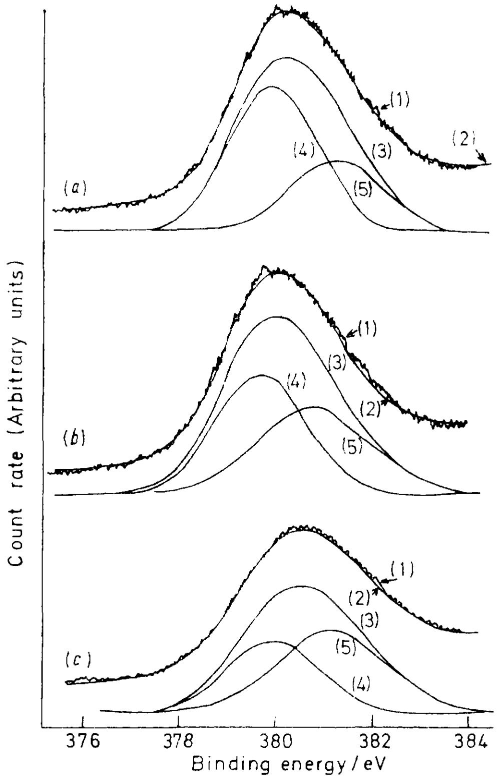

FIGURE 4 Curve-resolver studies of surface-oxidation effects on the uranium $4f_{7/2}$ line from the phase $UO_{2\cdot001}$: (*a*) and (*b*) powdered pellet immediately after grinding; and (*c*) powdered pellet exposed to air for a long time. In (*a*)—(*c*) curve (1) is the observed spectrum, (2) the best fit, (3) the best fit with sloping baseline removed; and (4) and (5) are component curves of (3). In (*a*) both component curves are $UO_{2\cdot0}$ pellet peak shapes; in (*b*) and (*c*), (4) is a $UO_{2\cdot0}$ pellet peak shape, (5) a U_3O_8 peak shape

the pellets were erratic, which is not surprising since this is far from a controlled oxidation experiment.

Summarising, the results show that grinding the sintered pellets in air causes oxidation, and that prolonged exposure of the powder to air oxidises the sample further. The fact that on heating the powders at 800 K under vacuum the uranium 4*f* binding energies do not become lower than values for the $UO_{2\cdot001}$ pellet is strong evidence that these latter values are characteristic of ' pure ' UO_2. The surface oxide structure responsible for the broadening effects may arise from several processes which can be generalised into two alternatives. Either a new oxide grows as a separate phase from the UO_2 phase, or excess of oxygen is incorporated into interstitial sites in the lattice to form a surface phase of $UO_{(2+x)}$. In the former alternative the new oxide may be a known oxide such as U_4O_9, U_3O_7, U_3O_8, or UO_3, but because of the relatively small shift caused by surface oxidation the spectra can be only partially due to any new oxide, presumably forming a very thin or incomplete layer on the UO_2 surface.

The positions and peak heights of two Gaussian curves which closely approximated to the $UO_{2\cdot001}$ peak shape [Figure 3(*a*)] were varied until the best fit to the peak shape of the surface-oxidised specimen [Figure 3(*b*)] was obtained. The result can be seen in Figure 4(*a*). Interestingly, the peak-to-peak separation of the component curves is 1·3 eV and the lower-binding-energy component occurs at 379·9 eV, close to the observed binding energy of the $4f_{7/2}$ state in the phase $UO_{2\cdot001}$. The separation of 1·3 eV is slightly larger than the measured difference of 1·0 eV between the oxides UO_2 and U_3O_8, but is close to the value of 1·2 eV obtained by similar curve-resolver studies on the UO_2–U_3O_8 spectrum (see above). However, 1·3 eV is less than the chemical shift between the oxides UO_2 and UO_3 (see Table). On repeating the exercise using a Gaussian curve approximating to the broader U_3O_8 peak shape, the peak-to-peak separation was reduced to 1·1 eV [Figure 4(*b*)]. Similar studies on the spectrum of the powdered sample, which had been exposed to air for a long period, produced a separation of 1·2 eV, the lower-binding-energy component occurring at 380·0 eV [Figure 4(*c*)].

The above study indicates that broadening of the uranium photoelectron peaks can be explained in terms of growth of a new oxide to an extent that does not completely suppress the UO_2 spectrum. The peak-to-peak separations point to the oxide U_3O_8 being present, but the 4*f* binding energies in U_4O_9 and U_3O_7 are only 0·3 eV lower than that in U_3O_8. Also, since the peaks in the oxides U_4O_9 and U_3O_7 have a greater linewidth than that in U_3O_8, allowance for this in the deconvolution studies would tend to decrease further the resolved-components separation.

The possibility that the surface-oxidation product is a fluorite phase $UO_{(2+x)}$, with the excess of oxygen occupying interstitial sites, would not be expected from consideration of the phase diagram. However, if such a phase were stable at the particle surfaces, it must reach $UO_{2\cdot2}$ after prolonged exposure to air, on the basis of the observed half-width. It could be argued that, if there was a concentration gradient of interstitial oxygen in the particles, greater than the escape depth of the photoelectrons (less that 50 Å), a greater broadening effect than for a homogeneous phase would have been observed in the *X*-ray/p.e. spectra. Alternatively, the extent of surface oxidation may vary from particle to particle. Thus, the *X*-ray/p.e. results alone do not identify with certainty the surface oxide structure although they narrow the field. On the other hand, *X*-ray diffractometer traces did not distinguish between the pellets or powders, even after prolonged exposure of the latter to air, which underlines the surface nature of the oxidation.

Satellite Peaks.—One feature of the uranium 4*f* doublets not considered in the above discussion is the appearance of small satellites which lie to the high-binding-energy side of the main peaks. In Figure 2 the satellite associated with the $4f_{7/2}$ peak was observed in all the spectra, particularly that of the oxide $UO_{2\cdot0}$ (the satellite associated with the $4f_{5/2}$ component is not reproduced) and its position varied somewhat within the range 6—8 eV above the main peak. The weak satellite in the U_3O_8 spectrum was quite reproducible. These lines are probably associated with discrete energy losses from certain photoelectrons by ' shake-up ' processes [22–26] which are caused by the sudden changes in effective charge that accompany ejection.

The separation of the satellites from the main peaks has been determined to be 6·9 and 7·8 eV for the oxides $UO_{2\cdot0}$ and U_3O_8 respectively, using the curve resolver. Disappearance of the satellites in the crushed pellet specimens may be explained by growth of new oxide at the surface. In this event, a very broad satellite with low intensity would occur and may be undetected. In a classical semiconductor, the minimum possible separation of a ' shake-up ' satellite from the main peak is the band gap (from the top of the valence band to the bottom of the conduction band). On the other hand, the observed separation must represent a *maximum* value for the band gap in these compounds. Estimates of the band gap in the oxide UO_2 vary widely, but a value of not less than 5·25 eV, determined spectroscopically, appears to be the most reliable.[27] Thus, the true energy gap in UO_2 must lie between 5·25 and 6·9 eV.

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