Auger Spectroscopy of Uranium

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Uranium metal and oxidised uranium metal surfaces have been examined by use of Auger electron spectroscopy. The methods used to obtain clean and oxide-free uranium metal surfaces are discussed together with the changes in the Auger spectra on oxidation. Chemical shifts in the uranium Auger peak positions resulting from changes in the electron energy levels in neutral uranium and uranium(IV) have been predicted by use of the electron binding energies determined by X-ray photoelectron spectroscopy.

AUGER electron spectroscopy as developed by Weber and Peria[1] has been used widely to determine the surface elemental composition of metals, semiconductors, and insulators. Recently attention has been focused on the application of this technique to the measurement of changes in the binding energies of electrons. These changes which accompany alterations in the molecular environment of atoms can be used to detect and identify surface compounds. In terms of the electronic structure of the substances investigated the Auger technique does not offer any improvement over *X*-ray photoelectron spectroscopy. Nevertheless with the advent of instruments offering chemical analysis in combination with electron microscopy Auger spectroscopy becomes particularly attractive by virtue of its ability to examine small cross-sections of material present in monolayer quantities. Moreover, the capability for recording spectra very rapidly, in fractions of a second, makes it valuable as a technique for studying the kinetics of reactions at surfaces. For these reasons it is important to characterise the changes which occur in Auger spectra of elements when combined with others to form compounds.

Somorjai[2,3] has shown that the Auger peak at 475 eV from the *LMM* transition in vanadium shifts to lower energy when vanadium is oxidised. In addition it has been observed[4] that the shape of the carbon peak at 272 eV shows a differing profile for graphite, diamond, silicon carbide, and Mo_2C. These variations have been attributed to different types of chemical bonding for the different forms of carbon.

Ellis and Campbell[5,6] have reported an Auger study of uranium and uranium dioxide. Their results were concerned primarily with uranium dioxide for which an assignment of orbital energy levels was attempted by using the uranium Auger transitions observed in the energy range 0—300 eV.

A brief account of our work on the chemical shifts observed in the uranium Auger peaks in the range 60—110 eV which accompany the oxidation of uranium metal has been given.[7] The results were obtained by use of a retarding field analyser[8] and we have extended this work by using a cylindrical mirror analyser concentrating our attention on the uranium Auger peaks observed in the range 45—115 eV and 225—315 eV. These peaks are considered to result from Auger transitions involving the valence band.

EXPERIMENTAL

Natural uranium metal, *ca.* 0·25 mm thick, was cut to shape for mounting in the ultra-high-vacuum system and electropolished in a solution of 33% H_2SO_4–33% H_3PO_4–33% H_2O to a thickness *ca.* 0·12 mm. After the sample had been mounted the vacuum in the apparatus was reduced to 1×10^{-8} N m^{-2} following baking at 500 K for 12 h. The surface of the uranium metal was examined by use of Auger electron spectroscopy.[8]

In this work a Vacuum Generators Ltd cylindrical mirror Auger analyser was used and this led to a considerable improvement in resolution when compared with the retarding field analyser used in the earlier work.[7]

Studies at elevated temperatures were carried out by direct current heating of the sample and the temperature was determined with a disappearing-filament pyrometer.

The uranium metal was oxidised at room temperature in an oxygen pressure of 1×10^{-5} N m^{-2}. This allowed sufficient time for Auger spectra to be taken at all stages during the oxidation process. Argon-ion sputtering was carried out with a Vacuum Generators AG1 500 eV argon-ion gun.

RESULTS

The Auger spectrum of the untreated uranium metal surface, recorded at a pressure of 1×10^{-8} N m^{-2}, is shown in Figure 1(a). Oxygen and carbon are readily characterised by their *KLL* shell transitions which are observed as major peaks at 512 eV and 272 eV respectively. Similarly, the surface contaminants phosphorus, sulphur, potassium, and calcium can be identified by their respective *LMM* shell transitions at 120 eV, 150 eV, 250 eV, and 290 eV. The remaining peaks at 75 eV, 83 eV, 93 eV, 105 eV, and 185 eV are considered to arise from uranium Auger transitions.

After the uranium metal had been heated to 1070 K for a few minutes the Auger spectrum shown in Figure 1(b) was recorded. The oxygen peak previously observed at 512 eV was not evident in this spectrum but a marked increase in the intensity of the respective sulphur and phosphorus peaks at 150 eV and 120 eV had occurred. Since sulphur and phosphorus are present as impurities in uranium metal

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[5] B. D. Campbell and W. P. Ellis, *J. Chem. Phys.*, 1970, **52**, 3303.

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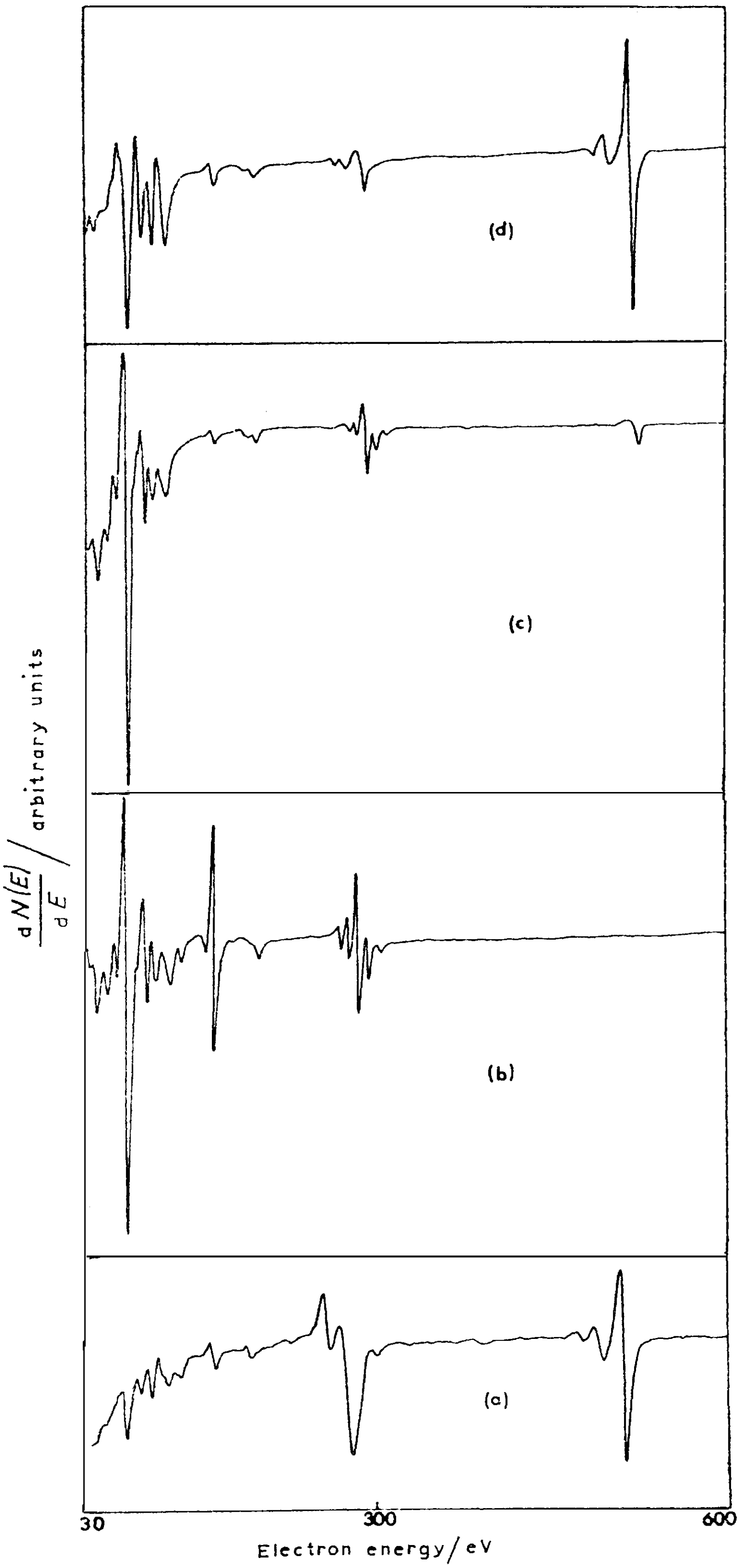

FIGURE 1 Auger spectra from uranium metal foil (a) as received; (b) after being heated to 1170 K *in vacuo*; (c) after oxidation followed by heating in hydrogen; (d) after exposure to oxygen

this observation is consistent with the diffusion of these elements from the bulk of the sample to the metal surface. Both the sulphur and phosphorus peaks were found to disappear when the sample surface was bombarded with argon ions but since a 500 eV argon-ion gun was used in the experiment the process required *ca.* 30 min during which time a small oxygen peak built up. The oxygen peak could be removed by further heating but again the sulphur and phosphorus peaks were observed. A further complication in this work arises from the fact that UO_2 is a particularly stable oxide ($\Delta H = -509$ kJ mol^{-1}) so it is likely that the oxide-free surface was produced by diffusion of the metal through the oxide layer to the surface. Consequently, repeated argon-ion bombardment followed by heating produced a uranium metal containing a high concentration of oxide with the result that after a number

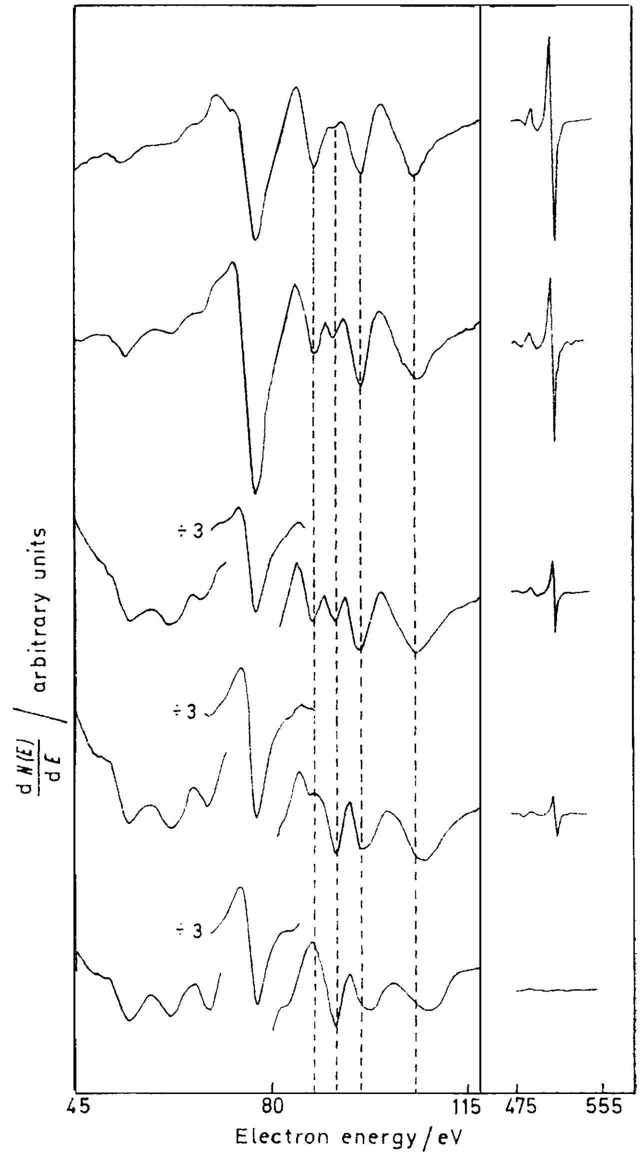

FIGURE 2 Auger spectra from uranium metal foil as a function of oxygen 515 eV Auger peak height

of bombardment–heating cycles an oxygen peak was permanently observed.

A solution to this problem was found by taking a fresh sample of the ' as received ' uranium metal and heating to 1070 K to give the spectrum shown in Figure 1(b). The surface was then oxidised by admitting oxygen to the system at 10^{-5} N m^{-2}. After 30 min at this oxygen pressure the system was evacuated to 10^{-8} N m^{-2} whereupon hydrogen was admitted to give a pressure of 10^{-5} N m^{-2} for 10 min and the system re-evacuated to 10^{-8} N m^{-2}. The spectrum recorded from this specimen is shown in Figure 1(c). As the Figure shows only extremely small peaks due to oxygen and sulphur and no peak due to phosphorus was observed, and although the surface could not be obtained in a condition completely free from impurities, the impurity concentration was so small that in the ensuing discussion this spectrum is taken to be characteristic of ' oxide-free ' uranium metal.

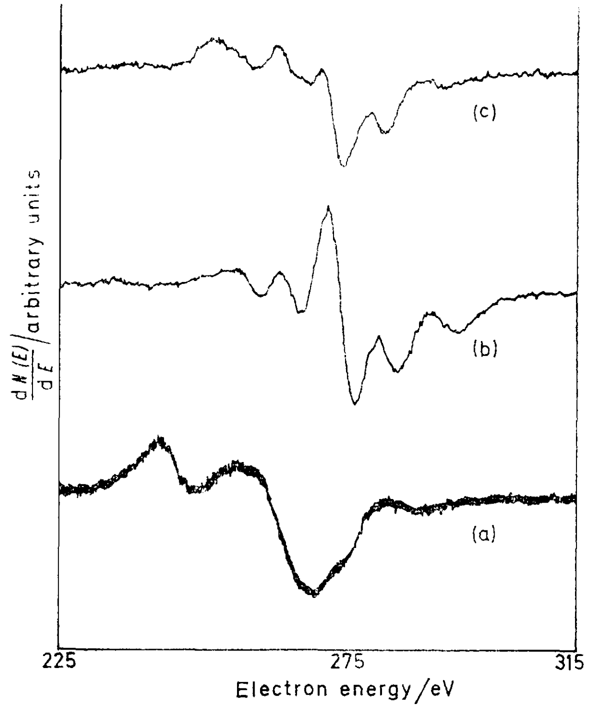

FIGURE 3 Auger spectra from uranium metal foil (a) as received; (b) after being heated to 1170 K *in vacuo*; (c) after exposure to oxygen

The uranium metal surface produced by heating the ' as received ' metal which gave the Auger spectrum shown in Figure 1(b) was not subjected to argon-ion bombardment but was exposed at room temperature to an oxygen pressure of 1×10^{-5} N m^{-2} for 2 h. From this specimen the Auger spectrum of the oxidised surface shown in Figure 1(d) was obtained. Numerous changes resulted in the energy range 45—115 eV and 225—315 eV and these are now discussed.

Auger Spectra in the Energy Range 45—115 eV.—A series of Auger spectra were recorded in the energy region 45—115 eV at regular intervals during exposure of oxide-free uranium metal to an oxygen pressure of 1×10^{-5} N m^{-2}. These are in Figure 2. The spectrum in the range 45—115 eV is illustrated on the left-hand side of the Figure and the region containing the corresponding oxygen peak is shown on the right-hand side. The Auger spectrum from the oxide-free uranium surface consists of an intense well defined gaussian peak at 75·5 eV, three less intense peaks at 53·0, 60·3, and 89·9 each having a width at half-height of *ca.* 4 eV, and two broad peaks at *ca.* 95 and 106 eV.

As oxidation proceeded changes in the shape and position of several peaks were observed. In particular the peak at 75·5 eV reduced in intensity and became considerably distorted towards the low-energy side and after complete oxidation it was possible to detect a new peak occurring at 70·5 eV. The peak at 89·9 eV retained its shape but showed a considerable reduction in intensity. Correspondingly a new peak was observed at 85·2 eV which increased in height as the 88·9 eV peak decreased. Even after prolonged exposure to oxygen, however, a small peak was still detectable at 88·9 eV. The broad peak in the 95 eV region sharpened during exposure to oxygen and shifted to lower energy at 93·7 eV. Similarly the peak in the 106 eV region also sharpened to some extent and shifted to *ca.* 103 eV.

Auger Spectra in the Energy Range 225—315 eV.—Auger spectra in the energy range 225—315 eV are shown in Figure 3. The spectrum recorded from the ' as received ' uranium after mounting in the spectrometer is shown in trace (a). Essentially this consists of three broad peaks at 250 eV, 272 eV, and 290 eV. The peaks at 250 eV and 290 eV can be assigned to the *LMM* shell transitions in potassium and calcium respectively, while the peak at 272 eV results from the *KLL* transition in the carbon atom. Transitions due to the uranium atom are masked by these impurity peaks although the most intense uranium transition was just detectable as an inflection at 278 eV to one side of the intense carbon peak.

After heating to 1070 K the spectrum shown in trace (b) was recorded. This spectrum is considered to be representative of that from oxide-free uranium metal. It consists of five peaks at 262, 269, 278, 285, and 295 eV, the most intense occurring at 278 eV. Each of the peaks had a half-height width of *ca.* 4 eV although at higher energy the peaks tended to broaden.

After exposure to oxygen for 2 h the spectrum shown in trace (c) was obtained from the surface. Again the spectrum was very different from that recorded from the oxide-free surface. The most intense peak at 278 eV shifted to 275 eV and showed considerable distortion to the low-energy side in a manner analogous to the peak at 75 eV described previously. The transitions at 285 eV and 295 eV also shifted by *ca.* 3 eV to lower energies but the peaks at 269 eV and 262 eV showed no significant movement. It could be argued that some of these transitions could be confused with transitions arising from carbon in a different state of chemical combination but experiments were carried out to ensure that this was not so. The process by which the spectra were obtained was completely reversible. Thus, the Auger spectrum obtained from oxide-free uranium metal could be regenerated from oxidised uranium by heating to 1070 K and conversely the oxidised uranium spectrum could readily be produced by exposure to oxygen.

DISCUSSION

The Auger process can involve as many as three electron shells. Accurately to predict the energy of an Auger electron emitted from an atom a precise knowledge of the binding energy of electrons in each of these shells is required. This is particularly important in atoms of high atomic number where a large number of electron shells are available for the Auger process. Moreover, the accurate prediction of changes in shape and position of the observed peaks in the Auger spectrum on oxidation requires some knowledge of the way in which the binding energy of the atomic orbitals change during this process. With this in mind we give below an assignment of the peaks observed from uranium metal and uranium dioxide in the energy region 45—115 eV. An assignment of the transitions observed in the higher energy region is complicated by the large number of possible transitions.

The binding energies of electrons in uranium metal and uranium oxide have recently been determined by Fuggle *et al.*[9] using *X*-ray photoelectron spectroscopy. These values are in Table 1. A comparison of these values with those of Bearden and Burr[10] reveals some disagreement between the values for the binding energies of the P_1, P_2, and P_3 levels. *X*-Ray photoelectron spectroscopy measurements of the uranium–uranium oxide system[11] carried out in our laboratory are in agreement with the values given by Fuggle *et al.* and therefore these values have been used to calculate the Auger peak positions in this work. Table 1 shows that the change in binding energy of the inner orbitals on oxidation is not constant. Changes ranging from 1·6 eV to 3·6 eV were observed.

TABLE 1

E.s.c.a. binding energies of orbitals in uranium metal and UO_2

	Metal	Oxide
O_2	258·4	260·8
O_3	194·8	198·4
O_4	102·8	104·9
O_5	94·2	97·1
P_1	43·9	46·2
P_2	26·8	29·0
P_3	16·8	18·4

The valence band also takes part in many Auger transitions. One normally considers the valence band to cover a fairly wide energy range yet the Auger transitions which appear to involve this energy level give peaks which are of similar half-height width to those in which the valence band plays no part. Clearly data providing information on the outermost levels in uranium are very valuable and as far as we know the only such data are those provided by Fuggle *et al.*[9] They observed a 2 eV shift in the valence band when the surface of uranium metal was allowed to oxidise. Moreover the valence band was observed to be relatively narrow with a half-height width of *ca.* 2 eV. For uranium the ground state of the neutral atom has the outer electronic configuration $5f^36d^17s^2$ and two $5f$ electrons are present in uranium(IV) compounds. Thus, whereas the $6d$ and $7s$ electrons can take part in Auger transitions in uranium metal only the $5f$ electrons are available for those transitions in oxidised uranium. In the absence of further information and for the purpose of calculating Auger transitions we have, following Fuggle *et al.*,[9] assumed here that the $5f$ levels in UO_2 lie 2 eV below the $7s$ level in the neutral uranium atom.

Calculation and Measurement of Auger Peak Positions.—A *KLM* transition in an atom of atomic number *Z* gives rise to an Auger electron with energy given by equation (1). This equation is not strictly accurate

$$E(Z)_{KLM} = E(Z)_K - E(Z)_L - E(Z)_M \qquad (1)$$

since after the initial hole has been created in the *K* shell the atom is in the singly ionised state. A more accurate value is given by equation (2) where Δ is the

$$E(Z)_{KLM} = E(Z)_K - E(Z)_L - E(Z + \Delta)_M \quad (2)$$

interpolation value between *Z* and $Z + 1$ and is generally between $\frac{1}{2}$ and $\frac{3}{4}$.

If equation (2) is to be applied to Auger transitions for uranium the electron binding energies for the element neptunium are required. These are not yet available, so the Auger electron energies are calculated here from the less accurate equation (1), and would therefore be expected to be somewhat greater than those observed. On the other hand Auger peak positions by convention are measured at the minimum on the d$N(E)$/dE curve. This does not correspond to the Auger peak maximum but to an energy *ca.* 2 eV greater. In view of this the peaks measured in this way and those calculated from equation (1) would be expected to have similar values.

The electron shell in which the primary vacancy occurs can be determined by varying the energy of the incident primary electron beam and noting the energy at which the peak under observation disappears. This experiment was carried out on both oxide-free and oxidised uranium metal. Peaks observed in the energy range 45—115 eV with a primary electron beam energy (E_p) of 2500 eV were still observable when E_p was reduced to 250 eV. Thus, the initially ionised electron apparently arises from one of the O_3, O_4, or O_5 electron

TABLE 2

Auger peak energies of uranium metal of UO_2

Metal			Oxide		
	Energy/eV			Energy/eV	
Transition	Calc.	Obs.	Transition	Calc.	Obs.
$O_3P_1P_1$	107·0	108·0	$O_3P_1P_1$	106·0	104·0
O_4VV	102·8	106·0	O_4VV	100·9	101·0
O_3O_5V	100·6	103·0	O_3O_5V	99·3	
O_5VV	94·2	96·5	O_5VV	93·1	93·7
O_3O_4V	92·0	94·5	O_3O_4V	91·5	—
O_4P_3V	86·0	89·9	O_4P_3V	84·5	85·2
$O_3O_5P_3$	83·8	—	$O_3O_5P_3$	82·9	
O_5P_3V	77·4	75·5	O_5P_3V	76·7	75·5
O_4P_2V	76·0		$O_3O_4P_3$	75·1	
$O_3O_4P_3$	75·2		O_4P_2V	73·9	70·5
$O_3O_5P_2$	73·8		$O_3O_5P_2$	72·3	
O_4P_1V	58·9	60·3	O_4P_1V	56·7	60·3
O_5P_1V	50·3	53·0	O_5P_1V	48·9	51·8

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[10] J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, 1967, **39**, 125.

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

shells. Further, energy-loss peaks in the region of the elastic peak were observed at **96** eV and **107** eV in agreement with the results of Ellis and Campbell[6] suggesting that the O_4 and O_5 levels are responsible for the majority of peaks observed in the **32—115** eV region.

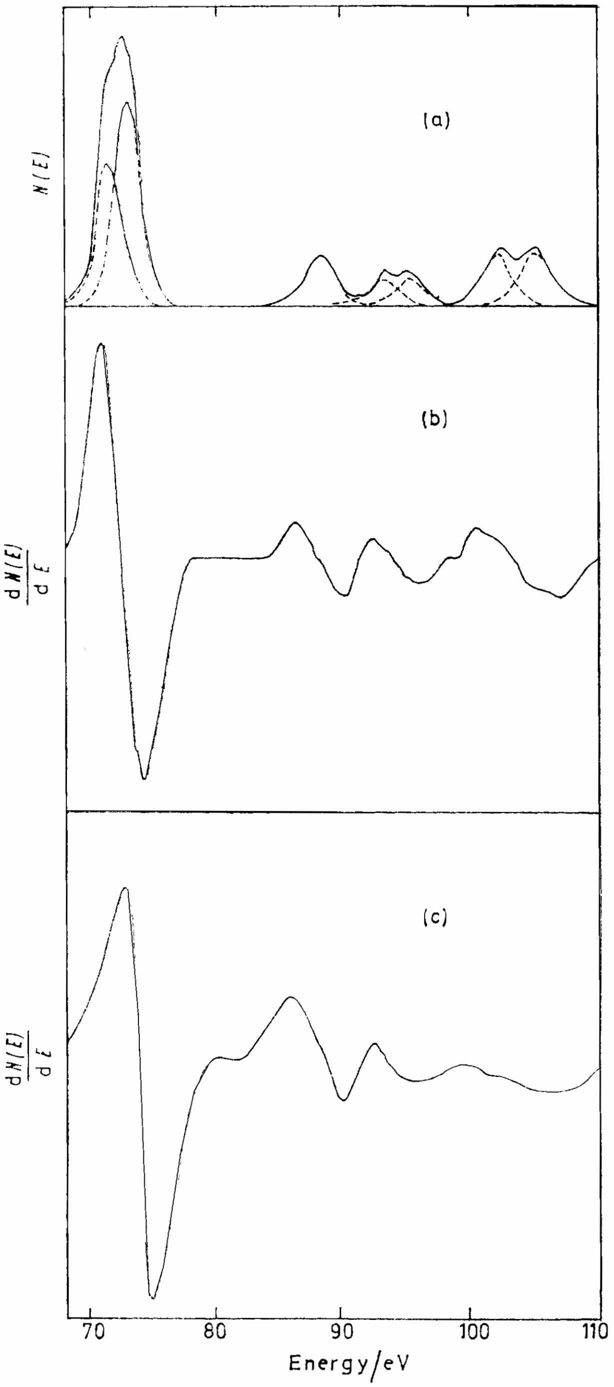

FIGURE 4 Reconstruction of Auger spectrum from uranium metal

Auger electron energies for which O_3, O_4, and O_5 levels are used as the initially ionised level are listed for oxide-free and oxidised uranium in Table 2. There is fairly good agreement between the calculated and observed values.

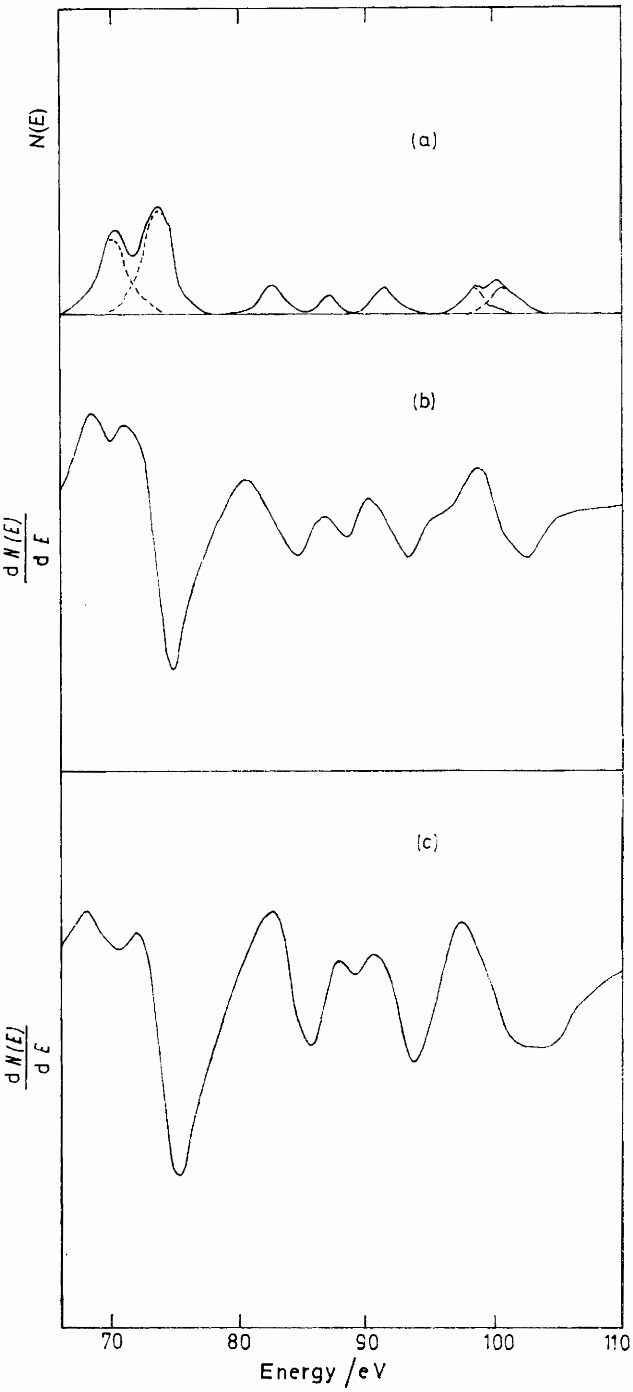

FIGURE 5 Reconstruction of Auger spectrum from oxidised uranium metal

No peak could be identified from uranium metal at 83·8 eV although from a theoretical standpoint a peak from the $O_3O_5P_3$ transition should occur in this position. Because this transition is not observed and since no energy-loss peak corresponding to the O_3 level could be identified it is considered unlikely that the similar transitions $O_3O_4P_3$ and $O_3O_5P_2$ at 75·2 eV and 73·8 eV occur. Thus, the peak at 75·5 eV is considered to be the result of the transitions O_5P_3V and O_4P_2V. By the same token it is also considered unlikely that the transitions $O_3O_5P_3$, $O_3O_4P_3$, and $O_3O_5P_2$ occur in the oxide.

An attempt has been made to reconstruct the observed spectrum by using gaussian peaks with a half-height width of 4 eV. Two peaks separated by 1·4 eV as measured by Fuggle *et al.* have been used for the 75·5 eV peak representing the O_5P_3V and O_4P_2V transitions.

The sharp peak at 89·9 eV has been reproduced by one gaussian peak while the broad peaks at 95 eV and 106 eV have each been reproduced by two gaussian peaks separated by 2 eV for the 95 eV peak and 3 eV for the 106 eV peak. This reconstruction is shown for uranium metal in Figure 4. The gaussian peaks are shown in Figure 4(a) together with the differentiation of this spectrum in Figure 4(b). For comparison the observed spectrum, corrected for the sloping baseline, is reproduced in Figure 4(c). There is good qualitative and fairly good quantitative agreement between the reconstructed and observed spectra.

By the same method the Auger spectrum for uranium oxide has been reconstructed with the following additional constraints. The relative gaussian peak heights used in the oxide were the same as those used to reconstruct the spectrum from the metal. The area under each peak was reduced to account for the reduced number of uranium atoms per unit area on the surface. The peaks producing the Auger peak at 75·5 eV in the uranium metal were separated by 4 eV and the remaining peaks shifted as shown to reproduce the spectra shown in Figure 5. Again the gaussian peaks are reproduced in Figure 5(a) and the differentiated resultant in Figure 5(b). The observed spectrum, corrected for the sloping background, is shown in Figure 5(c). Once more the qualitative agreement between the reconstructed and observed spectra is good and the quantitative agreement fairly good. It is encouragiug that the separation of the gaussian peaks required to produce the observed peaks at 75·5 eV in both uranium and uranium dioxide are separated by values predicted from the calculations using the results of Fuggle *et al.*

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