XPS STUDIES OF ACTINIDE MATERIALS

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SUMMARY

Applications of X-ray photoemission spectroscopy (XPS) to the study of actinide materials are reviewed. Examples discussed here include the band structures of thorium and uranium metal, the multiplet structure associated with the $5f$ electron states in oxides of the transuranium elements, the test for temporal configuration fluctuations in NpO_2, crystal field splitting of the U $6p_{3/2}$ level in a series of uranyl compounds, mixed oxidation states in Cf_7O_{12}, and a test for the participation of $5f$ electrons in bonding in a series of uranium compounds.

INTRODUCTION

High resolution X-ray photoelectron spectroscopy (XPS) is a recently developed technique, being scarcely more than ten years old. In those few years, the understanding of the technique has improved dramatically and XPS has found applications within many fields of science. Yet, application of the technique to the study of the electronic structure and properties of actinide materials has barely begun. Dramatic successes in the application of XPS to the study of electron bands in simple metals and transition metals and to the study of localized states in the lanthanides have provided the groundwork for studying electron states and properties in the actinides. In this review, we shall cite a few of the capabilities that have been demonstrated using the XPS technique and show how these capabilities are exploited for actinide materials studies. Specifically we shall include some discussion of (I) the band structures of thorium and uranium metals, (II) multiplet structure associated with localized $5f$ electron states, (III) electron core level measurements and their application to the measurement of oxidation state and valence mixing in intermediate oxide compounds, (IV) crystal field effects, (V) the determination of outer electron configuration using systematic intensity measurements, and (VI) configuration fluctuations.

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II. DISCUSSION

A. Band Structures

One example of the interplay between band theory and XPS data for actinides is the study of thorium metal.[1] Fig. 1 shows XPS results for thorium metal compared with the computed density of states.[2] The agreement here, where all electrons are itinerant, is good. Valence band data have also been reported for α-uranium metal [1] (see Fig. 2). The 5*f* electron states, believed to be relatively itinerant in this material, are apparently located close to the Fermi edge where they dominate the XPS spectrum (the 5*f* states have a larger XPS cross section than do the *s*, *p*, and *d* valence electrons). Detailed comparisons with theory are lacking because the complicated α-uranium crystal structure has discouraged theorists from carrying out the needed band calculations.

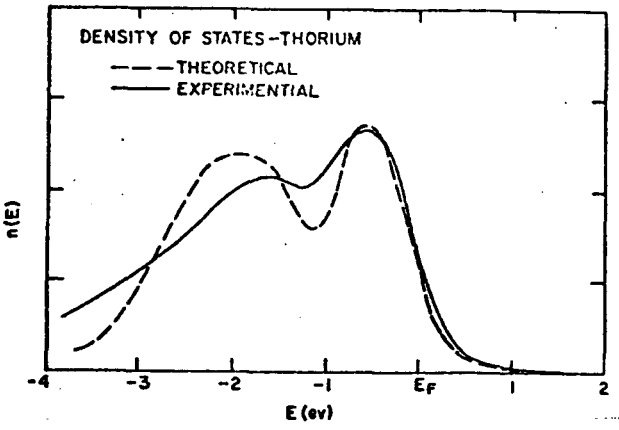

Fig. 1. XPS spectrum and the calculated density-of-states for thorium metal.

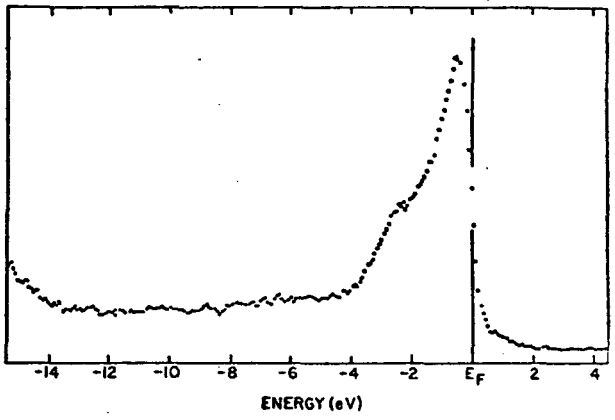

Fig. 2. XPS valence-band spectrum of α-uranium.

B. Localized States

1. Multiplet Structure

Single electron band theory can be applied to 5*f* electrons in the lighter actinide metals. For heavier metals (Z > 95) and for many actinide compounds, however, the 5*f* states are localized. For these states, one electron band theory is inappropriate. These localized states produce prominent effects in the XPS data which are unrelated to the occupied electron density of states. In the localized electron model, the XPS 5*f*-electron spectra may be understood in terms of the final state multiplet structure.[3]

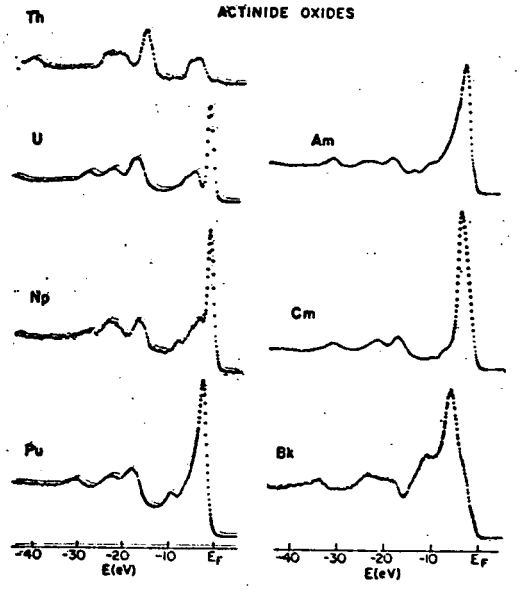

Fig. 3. XPS spectra for oxides of the actinides within 50 eV of E_F.

Fig. 3 shows XPS spectra within 50 eV of the Fermi level E_F for a series of actinide oxides spanning the range Z = 90 through 97. The three-peak structure centered around -25 eV is apparent in each of the oxides. These peaks are the An (actinide) $6p_{1/2}$, O $2s$, and An $6p_{3/2}$ lines, respectively. In ThO_2, at the lowest binding energy, only the O $2p$-derived covalent bonding electrons are observed. Comparison of the ThO_2 ($5f^0$) and UO_2 ($5f^2$) spectra provides clear identification of the localized $5f$ states. The $5f$ states produce the very prominent peaks near E_F. For increasing Z, the $5f$ spectrum acquires more structure and experiences varying degrees of linewidth, features resulting from the presence of multiplets in the XPS "final state" spectra.

Fig. 4 shows the XPS data for dioxides of neptunium, plutonium, and americium compared to the appropriate f^n multiplet calculation. [3] These multiplet spectra are dominated by the ground-state (atom) to ground-state (ion) transition.

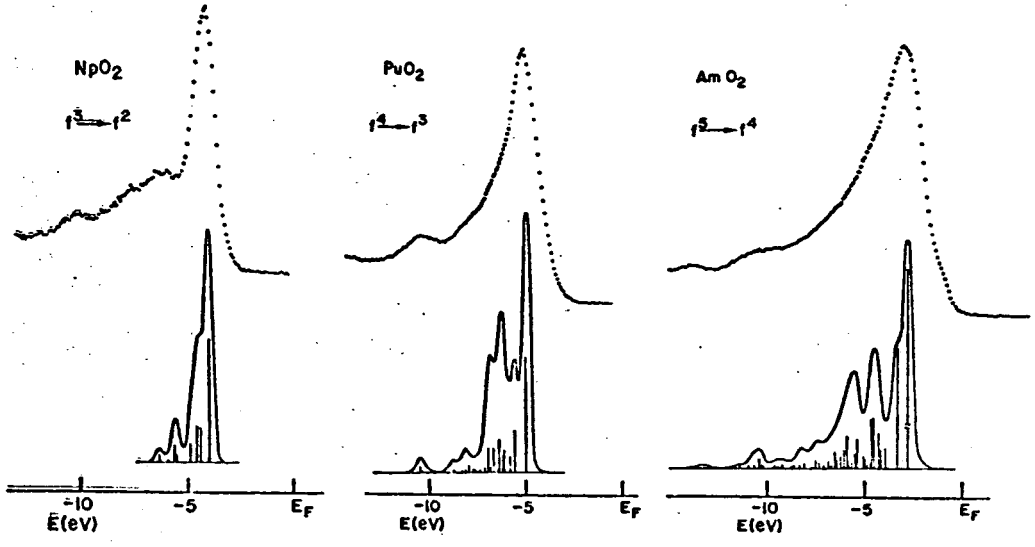

Fig. 4. Valence band XPS spectra and the calculated multiplets for dioxides of neptunium, plutonium, and americium.

This (lowest binding energy) peak was aligned with the dominant peak observed experimentally. Although the multiplet spectrum overlaps the bonding (predominantly O 2*p*) spectrum, the main peaks and some weak experimental structure can be correlated with structure in the calculated multiplet spectrum. The (initial state) f^6 configuration is the first (smallest f^n) in the oxide series for which the ground-state (atom) to ground-state (ion) transition does not dominate. This leads to a skewing of the leading (low binding energy) edge. Unlike the lighter oxides, this effect is seen in the curium oxide data of Fig. 3.

For the lighter actinides, thorium through neptunium, the dioxide is the lowest valence stable oxide. Beginning with plutonium, however, actinide sesquioxides can be prepared and their stability relative to the dioxides tends to increase with increasing atomic number. Although all samples were prepared using procedures devised to produce dioxides, it may be that because of sample preparation limitations or *in-situ* reduction, we were inadvertently measuring sesquioxides or intermediate oxides of the heavy actinides. The experimental spectra for the berkelium oxide along with the multiplet calculations appropriate for both the dioxide and the sesquioxide are shown in Fig. 5. The two sets of multiplet spectra compared to experiment do not clearly establish the oxidation state of the sample. The resemblance between the experimental spectrum and the calculated $5f^7$ spectrum, however, suggests that the sample is Bk_2O_3 or perhaps a mixture of the dioxide and sesquioxide. Comparable uncertainty exists for the oxide of curium.

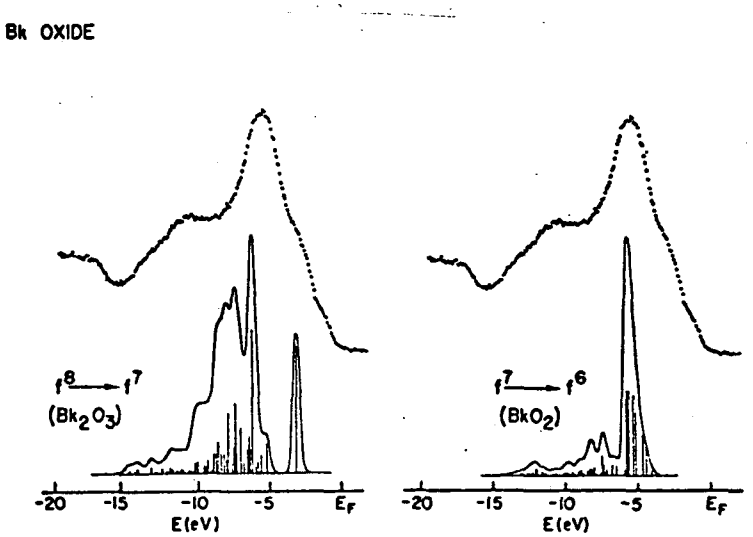

Fig. 5. Valence band XPS spectra for berkelium oxide compared with calculated f^7 and f^6 final state multiplets.

2. Configuration Fluctuations; the NpO_2 Problem

Another aspect of localized electron states which can be investigated with XPS is the possibility of fluctuations between different valence states. In the lanthanide compound TmSe, for example, temporal valence fluctuations have been invoked to explain anomalous

magnetic results. [4] The XPS results showed superimposed sets of multiplets which could be associated with the two proposed valence states. [5] Strong evidence confirming the existence of valence fluctuations was thus obtained.

The compound NpO_2 shows effects which are very similar to those of TmSe. Peaks in the magnetic susceptibility and specific heat at 25 K point toward antiferromagnetic ordering. The neptunium ion in NpO_2 should exist as $5f^3$ and thus should have a substantial magnetic moment in the ordered state. Yet the (ordered) moment, determined by Mössbauer and neutron diffraction studies, is less than $0.01\mu_B$. Unlike TmSe, the XPS spectra [6] for NpO_2, as shown in Figs. 3 and 4, do not confirm the valence fluctuation model. The $5f$ spectrum of NpO_2 is essentially a single narrow line. It is thus unlikely that the $5f$ electrons of NpO_2 are fluctuating between $5f^3$ and $5f^2 6d$ configurations (the TmSe analogy). For a fluctuating system, one would expect superimposed spectra corresponding to the individual configurations and separated by the correlation energy difference of the two configurations. [5] The conclusion that valence fluctuations do not account for the anomalous magnetic results is further reinforced by examing the integrated intensity of the combined valence band normalized to the integrated intensity of the oxygen $2s$ and actinide $6p$ lines in the three oxides. As shown in Fig. 6, the normalized intensity (with background subtracted) varies smoothly from ThO_2 to PuO_2. Since the magnetic properties of ThO_2, UO_2, and PuO_2 can be accurately described in terms of $5f^0$, $5f^2$, and $5f^4$, configurations, respectively [6], we see that the normalized intensity (Fig. 6) depends linearly on $5f$ electron occupation. These results indicate that the neptunium ions in NpO_2 are in the +4 state with the $5f^3$ configuration. The XPS data thus do not support the valence fluctuation model for NpO_2.

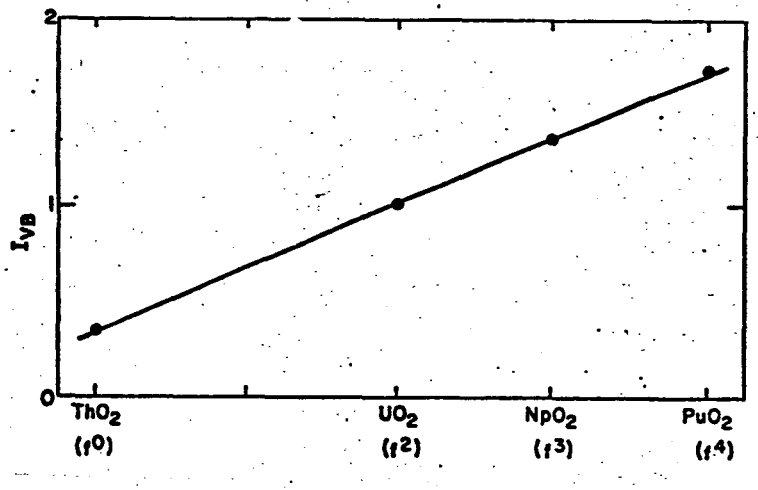

Fig. 6. The normalized integrated intensity of the valence electrons as a function of 5f electron occupation.

C. Crystal Field Effects

In a study involving more than twenty uranyl compounds [7], it was established that the axial crystal field within the uranyl unit can produce substantial

splittings in the XPS spectra of the actinide $6p_{3/2}$ core level. The uranyl is a very stable 3-atom linear chain UO_2^{++} group that exists in numerous compounds with varied crystal structures. The primary U-O separation in the uranyl unit ($U\text{-}O_I$) can be varied substantially, between 1.7 and 2.0 Å, by a suitable choice of compounds. The uranium-second neighbor distance is ($U\text{-}O_{II}$) ∿2.4 Å.

The $6p_{3/2}$ level, appearing as a single line in the compounds of Fig. 3 (the actinide dioxides have cubic symmetry), is split into two components in the axial electric field of the uranyl structure. Fig. 7 shows examples of the splittings observed in a sequence of uranyl samples with different $U\text{-}O_I$ separations. The experimental spectrum of those compounds with the smallest $U\text{-}O_I$ separation, including the U $6p_{3/2}$ splitting, is well represented by the characteristic energies obtained from a relativistic molecular cluster calculation. [8] The open circles of Fig. 8 show XPS data for the U $6p_{3/2}$ splitting observed in a number of uranyl samples plotted against $U\text{-}O_I$. The systematic trend of the data does not correlate well with the results of the cluster calculation (the triangles and the solid line). The cluster results fail for large

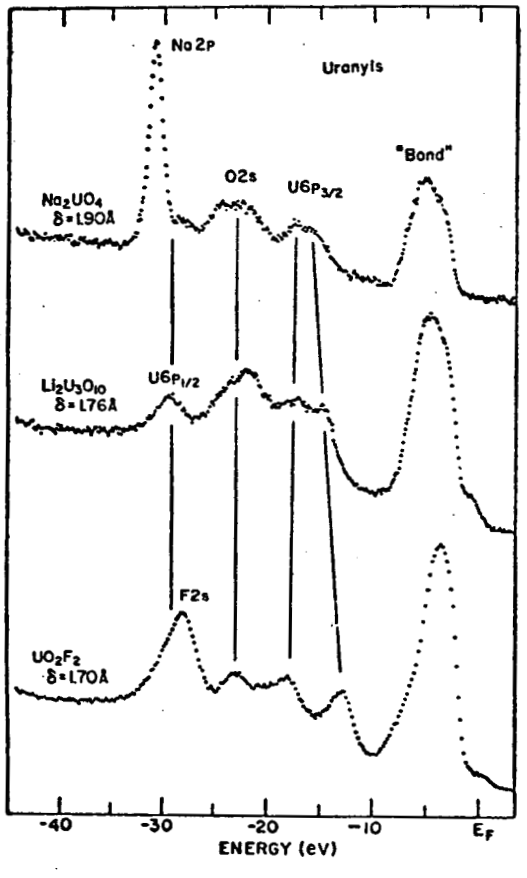

Fig. 7. XPS spectra for uranyl compounds showing the crystal field splitting of the U $6p_{3/2}$ levels.

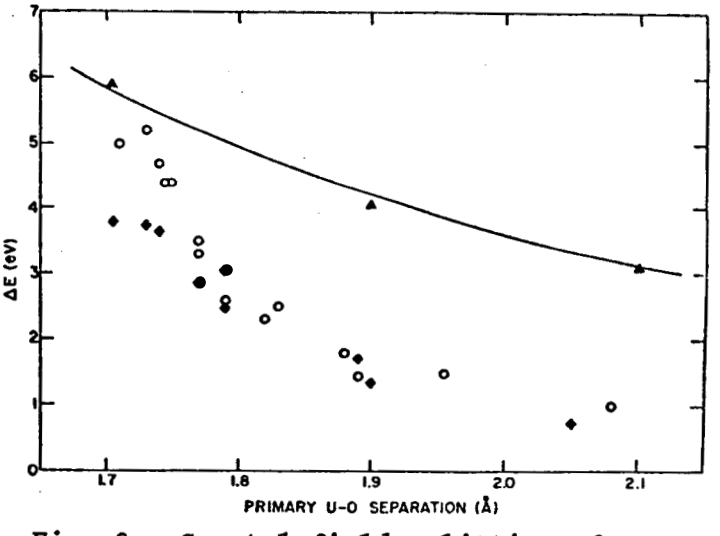

Fig. 8. Crystal field splitting of U $6p_{3/2}$ levels vs. $U\text{-}O_I$. The circles are XPS data and the line and triangles are cluster calculation results. The diamonds are corrected cluster results (see text).

$U\text{-}O_I$ because second-neighbor effects are neglected. Second-neighbor effects can be accounted for by utilizing a crystal field point charge model. Most of the uranyls studied have four oxygen atoms located on the equitorial plane for the uranyl group. For this structure, straighforward analysis yields the $6p_{3/2}$ splitting, $\Delta E_{3/2} = C(1/\delta^3 - 1/b^3)$, where C is a constant, $\delta = U\text{-}O_I$, and $b = U\text{-}O_{II}$. Using the value of C derived from the cluster calculation and using the measured values of δ and b, we obtain the solid diamonds shown in Fig. 8. These perturbed theoretical results now agree very well with the experimental results for all $U\text{-}O_I$. Thus the uranium near-neighbor effects and the second-neighbor corrections nicely account for the experimental observations.

D. Core Level Studies

One of the most important capabilities of the XPS technique is the measurement of absolute core level binding energies as a means of probing the local charge state of the ion under study. The oxidation state of the ion can sometimes be clearly discerned. An example is the XPS measurement for the intermediate oxides of uranium, U_3O_8 and U_2O_5, reported by Verbist et al. [9] Doublet structure in the U 4*f* lines was attributed to U^{4+} and U^{6+} ions since the 4*f* peaks appeared with nearly the same binding energies as the 4*f* lines in UO_3 and UO_2. Furthermore, the ratios of intensities of the separated peaks confirmed the assignments. Results very similar to those of the intermediate uranium oxides have been observed in Cf_7O_{12}. [3] The 4*f* lines are split, apparently into two chemically shifted sets of lines corresponding to Cf^{3+} and Cf^{4+} oxidation states. The ∿2.5 eV splitting of the Cf 4*f* levels is shown in Fig. 9. The O 1*s* level falls between the split $4f_{5/2}$ and $4f_{7/2}$ peaks.

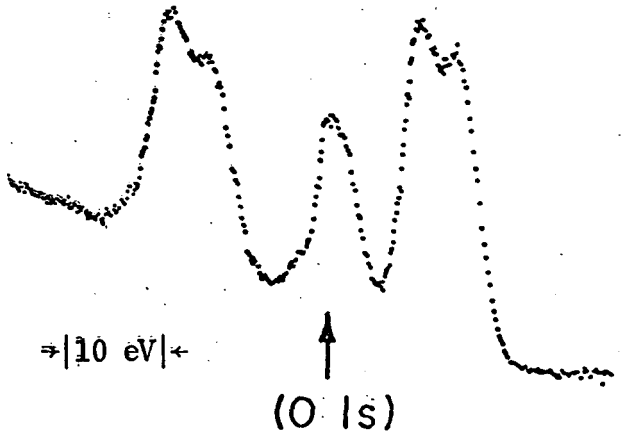

Fig. 9. XPS spectra for the 4f levels of Cf_7O_{12}.

Fig. 10 shows several core level energies for oxides of the actinides thorium through californium. In order to enhance the sensitivity in the display of the systematics of the core level energies, linear least squares lines were fit to the actinide core level data of Fig. 10. Fig. 11 shows the deviations between the experimental

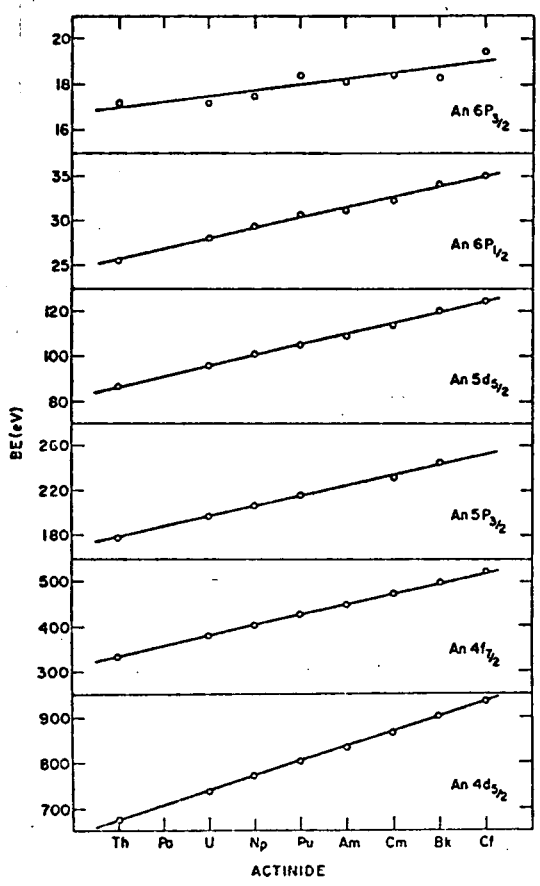

Fig. 10. Binding energies for several actinide core levels plotted vs. atomic number.

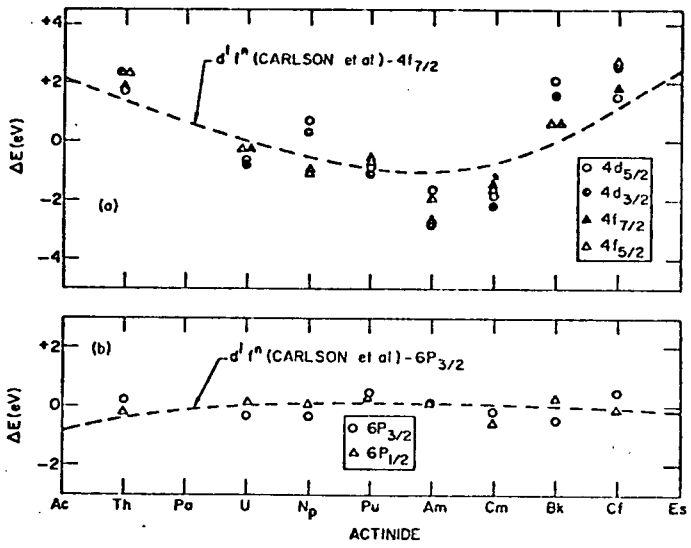

Fig. 11. Experimental and calculated (Ref. 10) deviations between core level energies and linear fits to those energies vs. atomic number.

4*d*, 4*f*, and 6*p* data and the corresponding linear least squares fits. Also shown in Fig. 11 are the deviations from a linear fit (chosen to pass through uranium and berkelium) to the relativistic theoretical results of Carlson et al. [10] for the $4f_{7/2}$ and $6p_{3/2}$ levels. The dashed lines in Fig. 11, representing the neutral atom calculations for the $4f_{7/2}$ lines, show the same general systematic behavior as is observed experimentally. Furthermore only a very weak (and opposite) curvature is seen for the low lying 6*p* levels which is again consistent with the experimental observations.

E. 5*f* Electrons and Bonding

Because of the strong sensitivity of XPS to 5*f* electrons (a U 5*f* electron has ∿6 times more intensity than a bonding O 2*p* electron), a capability is available for investigating the role of 5*f* electrons in covalent bonding. From symmetry considerations one might expect such bonding to occur between the oxygen 2*p* electrons and the actinide 5*f*'s. It was shown [12] in a study of the valence

bands of UO_2, U_3O_8, and UO_3 that the intensity of the localized U $5f$ peak (in UO_2 and U_3O_8) located near E_F can be chemically modulated by oxidizing the sample until, at UO_3, the peak has entirely disappeared (see Fig. 12). Since uranium is hexavalent in UO_3, all of the outer electrons of uranium participate in the covalent metal-oxygen bond. Apparently the $5f$ character is substantially lost when those electrons are drawn into the covalent bond by increasing the oxidation state. This result is further substantiated by a systematic study of valence band XPS intensities for a series of compounds in which the uranium/oxygen ratio is varied. We have systematically examined a series of covalent uranium-oxygen compounds with uranium valences spanning the range 4 to 6. [13] These chemical systematics monitor the transfer of $5f$ electrons from a localized level into the covalent bond. The intensity of the U $4f_{7/2}$ line should scale with the uranium concentration for a given set of experimental conditions and comparably prepared samples. The intensity of the bonding band (normalized to the U $4f_{7/2}$ line intensity) should scale with oxygen concentration only <u>if the bond is made up solely of</u> *p*-electrons. For this case,

$$I_{Bond}/I_{U\ 4f_{7/2}} \propto O/U. \qquad (1)$$

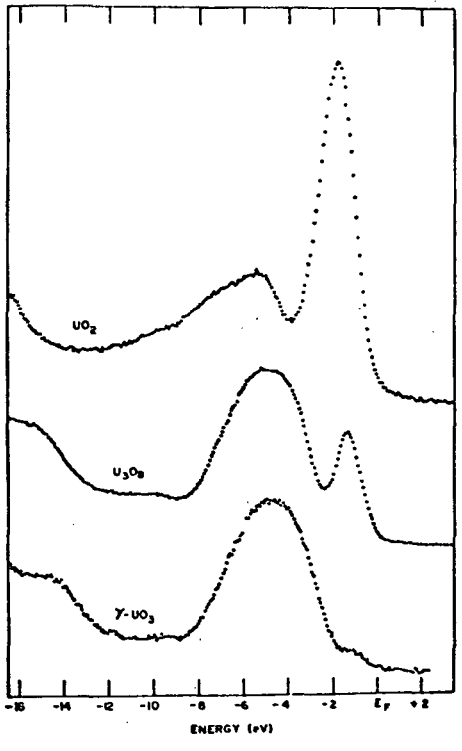

Fig. 12. XPS valence spectra of UO_2, U_3O_8, and γ-UO_3.

On the other hand, <u>if the $5f$ electrons participate in the bond</u>, then we can chemically modulate the number of $5f$ electrons in the bond simply by varying the uranium valence. For example, in UO_2, there are known to be two $5f$ electrons remote (in energy) from the bond and hence at most one $5f$ in the bond (the free uranium atom has three occupied $5f$ electrons). In UO_3, however, there are no $5f$ electrons outside the bond so that as many as three $5f$ electrons might appear in the bond. Since the intensities of the U $5f$'s and the O $2p$'s are very different, Eq. (1) should fail badly for $5f$ participation in bonding providing that the intensities of the covalent

5*f* bonding electrons are comparable to intensities of the 5*f* nonbonding electrons.

Fig. 13 shows $I_{Bond}/I_{U\ 4f_{7/2}}$ (solid line) plotted versus O/U for a series of compounds spanning the O/U range from 2 to 4. Within experimental error, we find that Eq. (1) is satisfied and even includes the point (0,0). Furthermore, when the 5*f* peaks are included in the integration (solid dots and dashed line), it is significant that the total valence band intensity actually decreases (between UO_2 and UO_3) even though the total number of electrons in the compound (per uranium atom) has substantially increased. Again, this indicates that the 5*f* electrons, when transferred from their localized nonbonding states to covalent bonding states, give up their 5*f* electron identity, at least insofar as XPS is able to discern it. Thus, it appears that 5*f* electrons participate minimally in covalent bonding. Rather, for the hexavalent uranium compounds, all 5*f* levels appear to lie above the fermi level.

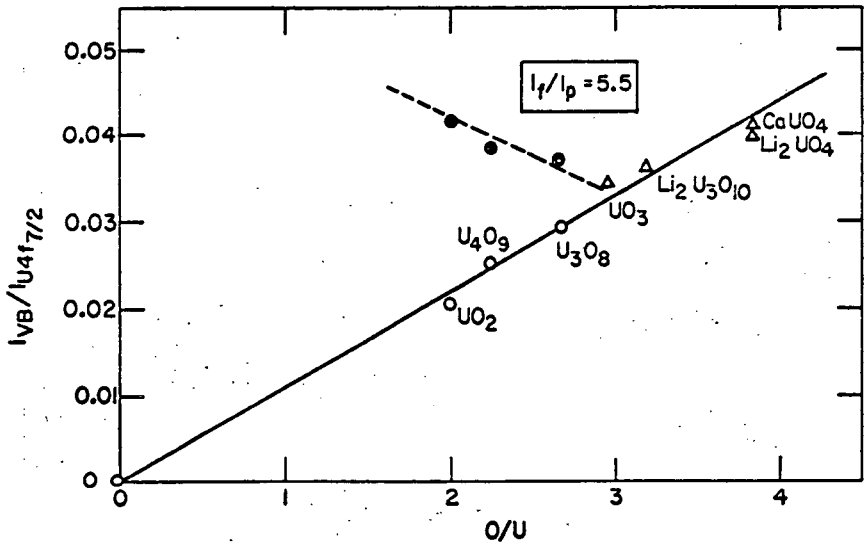

Fig. 13. The normalized XPS "bond" intensity (solid line) vs. O/U ratio. The dashed line includes the U 5f electrons.

CONCLUSIONS

Although the application of X-ray photoemission spectroscopy to the study of actinide materials is very recent, the utility of the technique for studying a variety of problems relating to actinide electronic structures has been demonstrated. Several examples of valence band and core level studies have been cited in this review. The XPS technique appears to be particularly powerful for the study of 5*f* electrons. It can provide significant insights into the character

of the 5*f* electrons, including their itinerant and localized behavior and their role in bonding.

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