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Variable-takeoff-angle x-ray-photoelectron-spectroscopy evidence for an electronically modified surface in α-Pu

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Photoemission spectra of an α-Pu surface taken at 15° and 85° off normal show pronounced changes attributable to an expanded δ-like surface layer. Using estimates for the inelastic mean free path of the photoelectrons and the thickness of the surface layer, we obtain spectra of the bulk and surface. The significance of this phenomenon is discussed within the context of the more familiar surface reconstructions that occur in the heavy transition metals. In contrast to the latter, the behavior of Pu is determined by the energy gain associated with $5f$ spin and orbital polarization rather than the increased cohesion that accompanies surface contraction.

I. INTRODUCTION

It has long been recognized that the reduced coordination number at the surface of metals can lead to altered spacing between the first and second layers and, in some cases, reconstruction of the outermost layer. The driving force for these phenomena can be understood as an attempt to minimize the total energy by increasing the surface atomic density with its attendant band broadening and increased band cohesion. The energy gain associated with the latter must compete with the energy cost of the loss of registry with the bulk and the transfer of material between the surface and bulk. In addition, there is a possible energy cost in loss of spin and orbital polarization; this will prove quite pertinent to our discussion of the plutonium behavior. Thus, although significant tensile strain exists in most metal surfaces,[1] significant structural changes are relatively rare.

Among the theoretical approaches which have been brought to bear on this problem are the embedded atom method[1] and total-energy monolayer calculations.[2] Each of these methods has found reasonable success in predicting the stability of a given surface to reconstruction, although some knowledge of the structure of the reconstructed surface is generally required. Total-energy calculations correctly predict the propensity of the Au(100) surface to reconstruct and its absence in Ag(100).[2] This methodology provides the useful insight that the relativistic energy lowering of the $6s$ level in Au effects stronger s-d hybridization than in Ag. The same situation exists in Pt and Ir, and is undoubtedly instrumental in driving the surface structural changes observed in these elements.

The unique position of Pu in the Periodic Table, as the last actinide element in which the $5f$ electrons contribute significantly to the bonding, is primarily responsible for its numerous unusual properties. The metal exists in six allotropic modifications with structures ranging from monoclinic (α and β) to fcc (δ) and bcc (ϵ). This manifestation of f itineracy in the lower temperature α and β phases is countered by peculiar electrical resistivity[3] and near magnetic behavior (although neither Curie-Weiss magnetism nor magnetic order is observed in any phase) which can only be interpreted as signaling atomiclike electronic correlation associated with incipient localization. That Pu should exhibit surface structural and electronic characteristics quite different from the transition metals is therefore a likely expectation.

The mechanism(s) responsible for the large-volume-change (approximately 19%) phase transitions in Ce and Pu is (are) not completely understood, and the inability of normal paramagnetic band theory to describe them accurately is well documented.[4–7] The added refinements of spin and orbital polarization have improved this situation (see following paper), at least insofar as they provide additional degrees of freedom with their concomitant reduction of f-band cohesion. The predicted existence of spin polarization at the surface of α-Ce (Ref. 8) is, for example, consistent with the observed[9,10] γ-like surface layer on both the former allotrope and several α-like intermetallics. In the case of Pu, state-of-the-art full-potential band calculations (see following paper) still significantly underestimate the α-phase lattice constant, a situation which would appear to require for its rectification a mechanism for reducing f bonding. It is clear that any theoretical model for the phase changes and surface reconstruction in Pu will have to account for the competition between f-band cohesion and atomiclike correlation which drives these phenomena. In this regard it would no doubt be useful to explore applying to Pu variants of the Kondo collapse model[11] and the Anderson Hamiltonian,[12] which have proved so successful for Ce materials.

It was shown previously[13] that dramatic changes in both the valence and core-level photoemission spectra of Pu accompany the α-δ phase transformation. In the $4f$ spectrum one observes large variations in the relative intensities of the spectral features arising from the well (f^6) and poorly (f^5) screened final states, which are primarily determined by lattice-constant-related $5f$-conduction-band hybridization. In addition to providing bonding information, the peak intensity ratio also yields a semiquantitative estimate of the volume occupied by a Pu atom in a particular environment. Thus the possibility of probing surface electronic structure via variable-take off-angle x-ray-photoelectron spectroscopy (XPS) suggests itself.

II. EXPERIMENT

The sample used in this study was a rectangular coupon of high-purity electrorefined Pu. Surface preparation was accomplished by mechanical and electropolishing, yielding a bright mirror finish. Some Ar-ion sputter cleaning was required to remove residual C- and O-containing contaminants. Unfortunately, the usual high-temperature annealing step which is carried out to remove sputter damage cannot be applied to Pu because of the phase changes which occur beginning at 120 °C. Cycling Pu through these transformations results in severe degradation of the surface finish as well as significant mechanical distortion. All sputtering and measurement were therefore carried out at 100 °C. That some sputter-induced damage undoubtedly remains under these conditions naturally engenders concern that the observed changes are artifacts. In a previous study of an α-Pu fracture surface,[14] however, we found $4f$ spectra which were very similar to those obtained in the present investigation. Specifically, the broad peak arising from the d-screened final state, which we show is mainly a surface feature, is present at about the same intensity regardless of the method by which a clean surface is obtained. It appears, therefore, that creating the modified surface layer involves little or no activation energy and does not require sputtering.

All variable-takeoff-angle spectra were obtained with a Mg $K\alpha$ x-ray source (1253.6 eV). Polynomial smoothing was applied to the data primarily to reduce noise in the difference spectra. Prior to generating difference spectra the background correction algorithm of Tougaard[15] was applied and the spectra were normalized using peak areas.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are the $4f$ spectra of α-Pu taken at 15° and 85°, respectively, off normal. The general features of this spectrum have been discussed previously.[13,14,16] Each of the spin-orbit-split components consists of a sharp feature at low binding energy representing a well-screened (f^6) final state and a much broader shoulder about 2.5 eV to higher binding energy resulting from a $6d$-screened (f^5) final state. The relative intensities of these features change dramatically between the α and δ phases of Pu because of the strong dependence on lattice constant of the $5f$-conduction-band hybridization. It is immediately obvious that the increased surface sensitivity of the low-takeoff angle (85°) spectrum causes a considerable increase in the f^5 feature at the expense of f^6 spectral weight. The latter feature also shows a small shift toward higher binding energy.

In order to compare more quantitatively the variable-takeoff-angle spectra with those of the Pu allotropes, it is useful to obtain, by difference, spectra representing only the bulk or the surface layer. This requires the assumption that spectra taken at different takeoff angles consist of linear combinations of the surface and bulk spectra, that the electron inelastic mean free path λ is not significantly different in the surface layer, and that the thickness of the latter is known. The contributions to the two spectra and the fractional contribution from the surface layer at a given takeoff angle (θ) are given by

$$S_{85}=fs_{85}\mathcal{S}+fb_{85}\mathcal{B}\ , \tag{1}$$

$$S_{15}=fs_{15}\mathcal{S}+fb_{15}\mathcal{B}\ , \tag{2}$$

$$fs(\theta)=1-\exp[d/\lambda^{*}\cos(\theta)]\ , \tag{3}$$

where S_{85} and S_{15} are the experimental spectra taken at

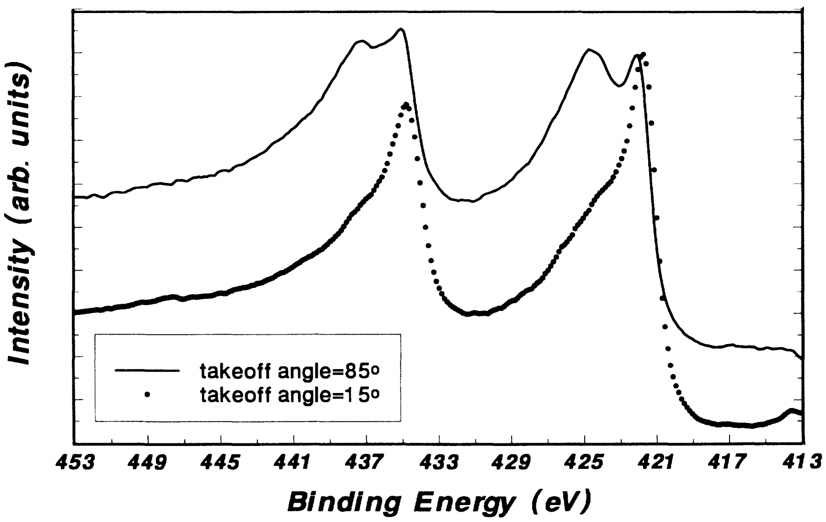

FIG. 1. $4f$ spectra of the α-Pu surface taken at 15° and 85° off normal, respectively.

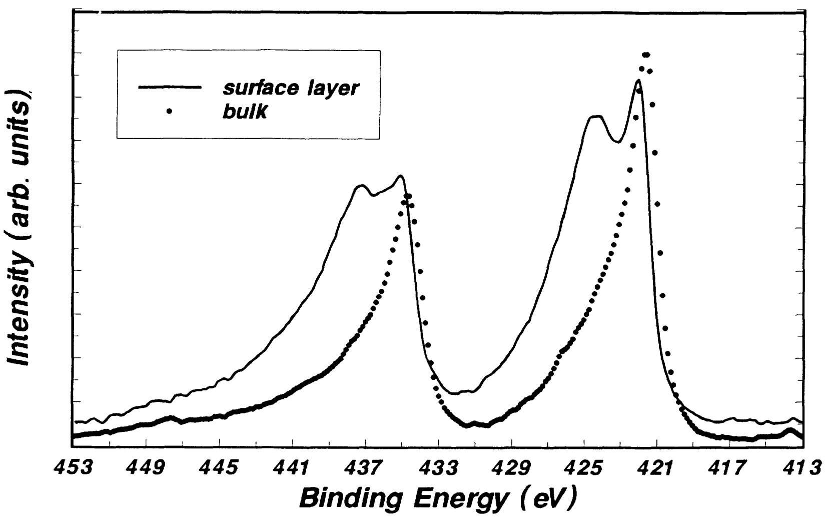

FIG. 2. 4f spectra of the bulk and altered surface layer of α-Pu obtained by difference. See text for subtraction procedure.

85° and 15°, respectively, off normal; fs_θ and fb_θ are the fractions of the experimental spectrum originating from the surface and bulk, respectively; and d is the nominal surface layer thickness. Solving Eqs. (1) and (2) for the spectra of the surface ($\mathcal{S}$) and bulk ($\mathcal{B}$) yields Eqs. (4) and (5):

$$\mathcal{S}=[(fb_{85}S_{15}/fb_{15})-S_{85}]/(fb_{85}fs_{15}/fb_{15}-fs_{85}) , \tag{4}$$

$$\mathcal{B}=[(fs_{85}S_{15}/fs_{15})-S_{85}]/(fs_{85}fb_{15}/fs_{15}-fb_{85}) . \tag{5}$$

Using an estimate of 1.27 nm for the λ of 820 eV electrons in Pu (Ref. 17) and $d=0.268$ nm one obtains $\mathcal{B}=S_{15}-0.215^*S_{85}$ and $\mathcal{S}=S_{85}-0.1107^*S_{15}$. The appropriately scaled difference spectra are shown in Fig. 2. The bulk spectrum exhibits pronounced asymmetry to higher binding energy and, although somewhat broader, is quite similar to those of Np (Ref. 18) and U.[19] Some small intensity remains at the position of the broad f^5 feature, but any accurate estimate of its area is precluded by the tailing of the main peak. Although the heights of the main peak and the shoulder are approximately equal in the surface spectrum, deconvolution suggests that the f^5 peak represents approximately 80% of the total area.

A comparison of the difference spectrum representative of the α-Pu surface and bulk δ-Pu at 380 °C is shown in Fig. 3. The width of the peak manifold is nearly the same for the two spectra, although more structure is evident in the δ-Pu spectrum, and the f^5 feature is sharper and more intense in the surface-derived spectrum. The essential similarity of the two spectra is compelling evidence, we believe, that the α-Pu surface is expanded and electronically similar to the fcc phase. XPS, unfortunately, provides no information about the physical surface structure.

As shown in Fig. 4, changes in the valence-band spectrum are also consistent with incipient 5f electron localization at the surface. As other studies have shown,[13,14,16] α-Pu exhibits a rather broad and featureless valence-band spectrum dominated by 5f-derived spectral weight. The existence of large f weight at E_f has been taken as evi-

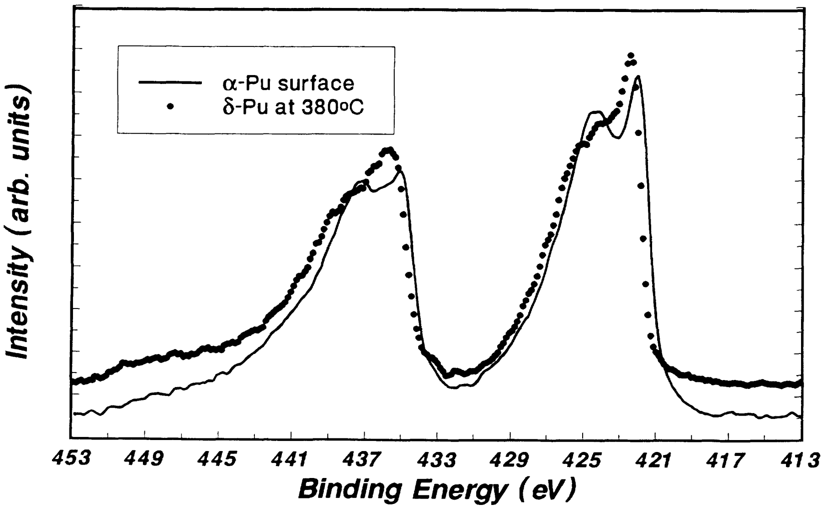

FIG. 3. Difference 4f spectrum representing the α-Pu surface and one of bulk Pu in the δ phase at 380 °C. The latter was obtained with a monochromatic Al k, α x-ray source.

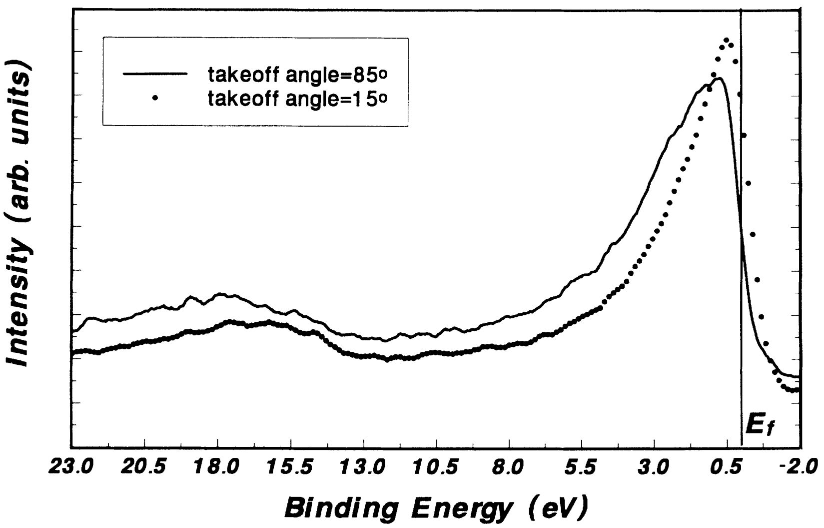

FIG. 4. Valence-band spectra of α-Pu taken at 15° and 85° off normal, respectively.

dence of f itineracy. Our preliminary results on β-Pu and γ-Pu (Ref. 20) show some increase in spectral weight at E_f, but a slight increase in bandwidth. This is contrary to the simplest interpretation in which the valence spectrum (corrected for cross sections and lifetime broadening) resembles a $5f$ density of states. A substantial decrease in the $5f$ bandwidth must result from the increase in lattice constant in the higher temperature phases of Pu. The most conspicuous evidence of many-body effects is seen in the δ phase for which photoemission shows the largest peak width, reduced spectral weight at E_f, and some suggestion of multiplet structure at higher binding energy.[13] All of these features are evident in the low-takeoff-angle spectrum as well.

The surface reconstruction of α-Pu is of particular interest because of the strong possibility that the same driving force is operative both here and in the five phase changes which occur in Pu below the melting point. The large lattice expansion (19%) and profound structural change (monoclinic to fcc) between the α and δ phases are among the most often cited of plutonium's peculiarities; however, it is less often noted that the enthalpy associated with the first three phase changes is only 0.05 eV. Thus, although the allotropes are superficially quite different, they do not differ much in metallic cohesion.

The inability of paramagnetic band calculations to account for $5f$ cohesion properly has been noted before.[4–7] This shortcoming is even apparent in full-potential, all-electron film-linearized muffin-tin-orbital (FLMTO—see following paper) calculations that were employed for the total-energy results shown in Fig. 5.[21] That $5f$ bonding is overestimated can be seen by comparing the minimum in the (bulk) total energy with the experimental values for the α- and δ-phase lattice constants. The energy difference corresponding to the α-δ volume change is also too large by approximately 0.5 eV. Both of these observations point to a reduction of f bonding presumably as a result of correlation effects. Of more significance for the problem at hand, however, is the fact that the energy minimum for a Pu monolayer is at a lattice constant 4.2% larger than the bulk. This is to be contrasted with the behavior of the heavy transition metals[2] in which significant contractions are found. The result for a spin-polarized calculation is also shown and, as expected, sub-

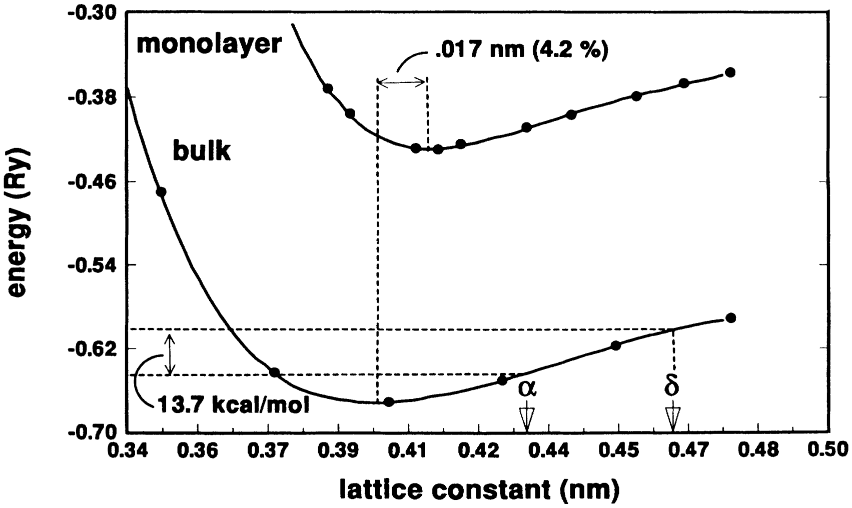

FIG. 5. Calculated total-energy curves vs lattice constant for bulk fcc Pu and for a Pu monolayer. The minimum energy for a spin-polarized monolayer is also shown. The experimental lattice constants for α and δ Pu are shown, as is the total energy difference between these volumes.

TABLE I. $5f$ band parameters for the center and surface layers from a five-layer slab calculation for Pu (100). C is the band center, E_v is the center of the occupied part of the band, n is the occupation number, W is the bandwidth, and $|n^*(E_v - C)|$ is an estimate (Ref. 22) of band cohesion. All values (except n) are in eV.

	Bulk		Surface	
	$j=\frac{5}{2}$	$j=\frac{7}{2}$	$j=\frac{5}{2}$	$j=\frac{7}{2}$
W	3.09	3.09	2.41	2.42
n	5.05		5.15	
E_v	−4.33	−4.50	−4.17	−4.38
C	−3.92	−2.88	−3.94	−2.90
$\|n^*(E_v-C)\|$	1.91	1.94	1.17	1.32
Total	3.85		2.49	

stantial further expansion is predicted. Although it is difficult to identify in detail the factors which lead to the predicted expansion of the Pu surface, they are presumably related to the attempt of (paramagnetic) band theory to mimic atomiclike correlation effects by increasing the $5f$ occupation of antibonding states. The following paper should be consulted for the details of the band calculations.

In forming metallic bands, Pu gives up its $5f$ spin-polarization energy at an energy cost of approximately 3.5 eV.[4] As shown in Table I, the estimated[22] $5f$ band cohesion is only slightly larger than this in the bulk and, due to an upward energy shift and band narrowing at the surface, drops well below it in the surface layer. Even though there is an additional energy cost because of the loss of registry, it is not at all surprising that the atomic expansion associated with $5f$ localization would be favored.

Except for the present study, there appears to be no published work on actinide surface structure or reconstruction except for the low-energy electron diffraction Auger study of Bastasz *et al.*[23] of the Th(111) surface. The latter reconstructs above 1000 °C to a bcc-like structure. $5f$ bonding is minimal in Th, however, so the driving force for its reconstruction is probably not related to that obtaining in Pu. If it is, in fact, the competition between spin-polarization energy and f-band cohesion that determines the propensity for an altered surface, then Pu may be the only actinide to exhibit this behavior. The spin-polarization energy increases rapidly along the series, and is accompanied by a less steep decrease in f-band cohesion. For U and Pu the spin-polarization energies are 1.35 and 3.47 eV, respectively, whereas the FLMTO-calculated[21] f-band cohesion for the surface layers are 2.99 eV (bcc U) and 2.49 eV (fcc Pu), respectively. Thus one would expect surface reconstruction due to f localization (i.e., a spin-polarized f band), as we believe occurs in Pu, to be unique to this element. One cannot rule out surface reconstructions in the lighter actinides, of course, but they are likely to be more subtle, and will likely be determined by changes in the relative importance of f and d bonding between the bulk and surface.

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