

Electronic structure of the (111) and (100) surfaces of δ -Pu

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An all-electron self-consistent surface-electronic-structure calculation of an actinide system has been performed using the film-linearized muffin-tin-orbital method. The calculations have been performed using both (100)- and (111)-oriented five-layer plutonium slab geometries. Our calculated work functions for the system are 3.68 and 4.14 eV for the (100) and (111) surfaces, respectively, with the $6p$ electrons treated as core states. The calculations include the spin-orbit coupling, and the calculated work functions are in good agreement with experimental values of 3.4–3.9 eV for uranium. The narrow bandwidth of the $5f$ electrons and the position relative to the s and d bands relate to the intermediate delocalization of the $5f$ electrons and the existence of hybridization with the s and d electrons.

I. INTRODUCTION

It is well known that the electronic behavior of the actinides varies widely.¹ The electronic-structure-based properties of the series vary from those of itinerant transition-metal-like systems to those of localized lanthanidelike systems. This behavior reflects that of the $5f$ electrons, which are believed to be itinerant and bonding in the early part of the series (Th–Pu) and atomiclike and localized for the latter elements in the series.¹ The radial extent of the $5f$ electrons is less than that of the $6d$ and $7s$ electrons. However, the tail of the $5f$ partial wave is much more extended than that of the $4f$ electrons in the lanthanides. Hence many light actinide systems form narrow $5f$ bands. These narrow $5f$ bands hybridize with the surrounding ligand states; and, in particular, for compounds this hybridization can be very important.²

Plutonium is unique among the elemental metals having six stable allotropes from room temperature to its melting point (~ 640 °C) at atmospheric pressure. The room-temperature α phase of plutonium is monoclinic. However, small amounts of certain impurities will stabilize the fcc δ phase (normal stability range 320 °C–450 °C) at room temperature. The δ phase is the only close-packed structure exhibited by plutonium, although with the lowest density among its six allotropes. For the lighter part of the actinides, from Th to Pu, the $5f$ electrons are in narrow bands which hybridize with the $6d$ and $7s$ electrons; while for the heavier part of the series, from Am on, the $5f$ electrons are localized.¹ Hence plutonium is located at the position where the electronic be-

havior is about to change from itinerant to localized. Since the bandwidths of surface states normally are narrower than those of the bulk, it might be that the crossover from delocalized to localized behavior has already taken place at the plutonium surface. One of the purposes of the work reported here has been to investigate this effect in detail. Thus the study of the electronic structure of the plutonium surface is very useful for the understanding of surface behavior in the whole actinide series. Through investigating the surface electronic structure one also obtains information useful for future studies of chemisorption and epitaxial growth on the Pu surface. The high atomic number of plutonium, and hence the importance of relativistic effects, makes the inclusion of spin-orbit coupling necessary. The surface-electronic-structure calculation of plutonium then becomes a very challenging and interesting task.

II. METHOD

We have used our recently perfected self-consistent film-linearized muffin-tin-orbital (FLMTO) method,³ which we have now extended to include spin-orbit coupling. The computational efficiency and high-quality results of the FLMTO method have been shown in a number of calculations of $3d$ and $4d$ transition metals.³ As a result of a systematic investigation to find a reasonable-sized basis that yields both high-quality results for surface properties and at the same time reduces computer time consumption to make such calculations practical, the FLMTO method has had great success in surface-

electronic-structure investigations of intermediate-sized atomic systems.³ An application to a very-heavy-atom system, however, is a new challenge, in part because we have to include f electrons and spin-orbit effects in the calculation.

The relatively small basis employed by the FLMTO method makes it possible to deal with a system of heavy atoms such as plutonium having f electrons and to include spin-orbit effects. The basis functions used here are a combination of the standard muffin-tin orbitals (MTO's) and of the plane-wave orbitals (PWO's) introduced for the FLMTO method together with the two-component spinors. The MTO's inside the sphere consist of a linear combination of the solution of the radial Dirac equation (neglecting the spin-orbit interaction) and its energy derivative for the spherically averaged potential at each iteration. We do not use the atomic-sphere approximation⁴ (ASA); the full potential is used everywhere except inside the muffin-tin spheres where the non-muffin-tin (NMT) potential is approximated by the extended interstitial NMT potential.³ In the interstitial region, the MTO is a Hankel function, while in the vacuum it is modified to be a linear combination of the solution of the one-dimensional Schrödinger equation and its energy derivative for the planar-averaged vacuum potential. The PWO's employed here are independent basis functions together with the MTO's. They treat the parallel (to the surface of the slab) behavior of electrons properly and yield results of desired accuracy for surface properties such as the work function, giving results comparable with experiment. The PWO's are two-dimensional plane waves in the direction parallel to the slab surface. Along the direction perpendicular to the surface, however, they either have a real exponential behavior or a plane-wave-like behavior, depending on the energy parameter and parallel reciprocal-lattice vector in the interstitial region. Like the MTO's, the PWO's are augmented inside the muffin-tin spheres where they take on the character of combinations of solutions of the spherical Dirac equation for the muffin-tin potential and their energy derivatives. In the vacuum they have the form of linear combinations of solutions of the one-dimensional Schrödinger equation for the vacuum potential and their energy derivatives. All these functions are continuous and have continuous first derivatives everywhere. In the present calculations, the exchange-correlation potential has been calculated using the Vosko-Wilk-Nusair parametrization⁵ in the local-density approximation. The core electrons have been treated fully relativistically by self-consistently solving the Dirac equation. The iterative calculations (both for core and valence states) have been carried out until the difference of input and output potential was of the order of a few mRy at all locations.

For the atoms of the plutonium slab, first the spherical potential problem is solved using the radial Dirac equation with the larger part of the relativistic effects, those due to the mass-velocity and Darwin terms, being treated properly, whereas the smaller spin-orbit term is neglected in the calculation of our basis functions. These semirelativistic (non-spin-orbit) effects were already included in previous versions of the FLMTO method.³ We then in-

clude the spin-orbit interaction $H_{s.o.}$ (defined below) at the variational step by diagonalization within the basis of functions that include the other relativistic effects (mass velocity and Darwin shift).^{4,6} The spin-orbit interaction, in this representation, can be written

$$H_{s.o.} = \left\langle \phi_{N\chi_s} \left| \frac{1}{2M^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} \right| \phi_{N'\chi_{s'}} \right\rangle, \quad (1)$$

where $\phi_{N\chi_s}$ are the basis functions, \mathbf{L} and \mathbf{S} are orbital and spin angular momentum, respectively, and V is the radial potential. This term is added to the Hamiltonian only in the sphere regions, where the spin-orbit interaction is appreciable.

The calculation is performed for a five-layer slab of plutonium with both (100) and (111) orientations. The slab surface is taken to be a plane with a two-dimensional lattice constant of 6.1963 a.u. (corresponding to the volume of δ -Pu).⁷ Since we have used z (direction perpendicular to the slab surface) reflection symmetry with respect to the center plane, we actually calculated for an $ABCBA$ stacking structure for the (111) surface (the effect of which is briefly discussed below). Because of the

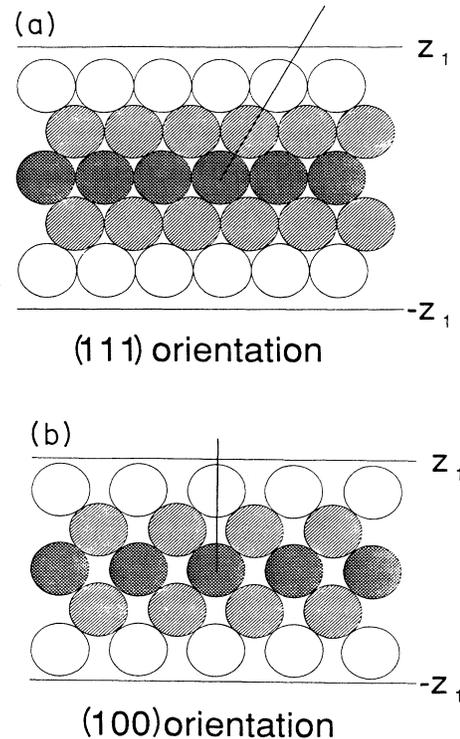


FIG. 1. Geometry of the five-layer plutonium slab (111) (a) and (100) orientation (b). The z direction is the direction perpendicular to the slab surfaces which are at z_1 and $-z_1$. The center atom is cross hatched, the subsurface atom is hatched from right to left, and the surface atom is open. The thick lines indicate the direction in which a cut is made to plot the charge-density contour (Figs. 5 and 6).

relatively small basis, it is not necessary to reduce matrix sizes through use of reflection symmetry in the FLMT0 method, and we are completing the reprogramming eliminating this restriction. The geometries of the (111) and (100) films are shown schematically in Fig. 1. The system includes five plutonium atoms (one for each layer) in a unit cell. Then, in the basis set, we have 80 MTO's (16 orbitals of s , p , d , and f character for each atom) and 14 PWO's. Thus both for the (111) and the (100) orientation, the matrix size is 94×94 , which becomes doubled for the spin-orbit coupling calculation, i.e., 188×188 .

One problem of the calculations is how to treat the $6p$ electrons since the radial extent of the $6p$ level is comparable to that of the $5f$ level. However, the $6p$ states are located at low energies and are completely filled. Therefore treating them as core electrons is a good approximation as has been shown earlier.⁸ To check on the effect of the treatment of the $6p$ electrons, we have tried two approaches, first forcing the $6p$ electrons to be localized and thus treated as core electrons, and then taking the $6p$ electrons as itinerant, i.e., we treat them as valence electrons. The correct way to treat the $6p$ levels would be to treat them as semicore states, i.e., to calculate them as filled band states in an energy window different from that of the valence levels, thereby avoiding orthogonalization problems, but this should make little difference in treating the $6p$ electrons as localized.

A special set of k points in the irreducible wedge of the Brillouin zone of the two-dimensional lattice⁹ has been used to obtain a good approximation to the density of states, the work function, and the charge-density distribution. A 6- (10-) point set gives accurate results for the (111) [(100)] surface while consuming acceptable computer time. In the FLMT0 method one chooses the kinetic energy of the envelope function and in principle this variational parameter should be optimized so that the total energy is minimized. Since this is quite tedious and time consuming we replace this procedure with the following one. For each iteration we calculate the center of mass of the density of states. The kinetic energy used in the basis function for the following iteration is set equal to this center-of-mass energy. This procedure is carried out iteratively until the final converged results are obtained.

Finally we comment upon convergence for the present calculation. In narrow band systems this is usually a big problem, since too large a mixing of the potential between two iterations results in instabilities, with oscillations in the charge density. An improvement is generally obtained by using more refined mixing schemes than simple linear mixing. In the calculation of the electronic structure of the (100) surface we improved further on the convergence by doing a calculation with the $5f$ states treated as core electrons. This calculation converges after ten iterations, and in each iteration we calculate the core density as well. The potential so obtained normally differs little from the one with the $5f$ states treated as bands and is therefore an excellent starting potential to use when including the $5f$ states in the valence band. Thus after ten iterations we have found the center of the $5f$ resonance, and then the inclusion of the $5f$ electrons in the band states converges fairly rapidly.

III. RESULTS AND DISCUSSION

A. Electronic structure of the (111) surface

Using the method described above we first self-consistently calculated the discrete energy eigenvalues and from them we calculated the density-of-states (DOS) curves by using a Lorentzian-broadening smoothing technique.¹⁰ Here we will discuss the results obtained with the $6p$ states treated as core states. The general character of the scalar relativistic (i.e., without spin-orbit interaction) DOS of the five-layer (111) slab (not shown) is that for a narrow band at the Fermi level superimposed on a broader type of state density with sd character. The bandwidth is ~ 0.95 eV for the surface and ~ 1.05 eV for the center, which are measured at half height of the DOS peaks. Similar to results for other surface calculations, the bandwidth of the surface is narrower than for the center, because a surface atom has fewer neighbors than a center one.

Sometimes it can be difficult to estimate the bandwidth from the width of the state density at half maximum. Another commonly used approach is to associate the bandwidth with the square root of the second moment of the density of states.¹¹ Since the second moment of the density of states to first approximation scales with the number of nearest neighbors, the bandwidth is expected to scale with the square root of the number of nearest neighbors if direct f overlap dominates the bandwidth behavior.¹² Bulk fcc plutonium has 12 nearest neighbors, whereas the surface coordination is only 9. Hence from these simple arguments the surface-to-bulk bandwidth ratio should be $\sqrt{9/12}$ or about 0.87, which agrees rather well with our computed value of 0.90.

Figure 2 shows the sphere-projected DOS of the calculation with spin-orbit coupling. The overall $5f$ bandwidth is wider than in the absence of spin-orbit coupling, with the $5f$ band being split into two distinct peaks separated by 1.3 eV, peak to peak, for both the atom at the surface and at the center. This splitting comes from the spin-orbit coupling. When decomposed into orbital-projected components, the DOS of the surface and center qualitatively show as the dominant feature the presence of two relatively narrow peaks corresponding to spin-orbit-split $5f$ bands straddling the Fermi level. The $5f_{5/2}$ peak is about 0.2 eV below the Fermi energy. The $7s$ and $6d$ bands are spread over a wide energy region and hybridize with the $5f$ bands, whereas the p band is almost empty, as expected since we treat the $6p$ state as a core state and thus pick up the high-lying $7p$ band in our valence state. The position of the $5f$ band relative to the $7s$, $7p$, and $6d$ bands implies overlap of the s , p , d , and f , orbitals, giving hybridization of the f orbitals with the d , p , and s orbitals, with the f - d hybridization being the most important. The orbital-projected charge distribution given in Table I suggests that approximately one and a half of the original atomic s electrons and approximately one atomic f electron are excited to d orbitals and to interstitial wave functions and to a lesser extent the p orbitals which are empty in the atomic state (the atomic configuration is $7s^2 5f^6$). These numbers should not be

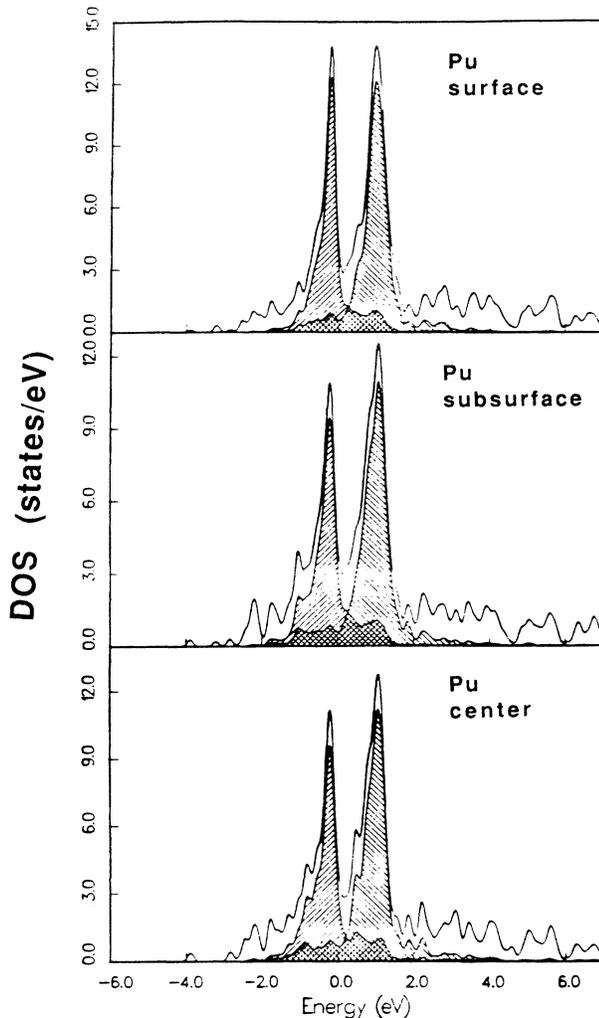


FIG. 2. Sphere-projected density of states from the (111)-relativistic calculation (with spin-orbit interaction). The area under the $5f_{5/2}$ partial density of states is hatched from left to right whereas the area under the $5f_{7/2}$ density of states is hatched from right to left. The three panels show the density of states from the center, subsurface, and surface atoms, respectively. Energies are in eV and the Fermi energy is at zero.

treated as unique, since to some extent they depend on the choice of the muffin-tin sphere. However, the amplitude of the $5f$ wave functions is low at the muffin-tin sphere boundary, making the $5f$ occupation relatively insensitive to this choice.

In Fig. 2 we also plot the $5f_{5/2}$ (hatched from left to right) and $5f_{7/2}$ (hatched from right to left) projected DOS's. Figure 2 shows the $5f_{5/2}$ peak 0.2 or 0.3 eV below the Fermi level. The Fermi level cuts the high-energy side of the $5f_{5/2}$ peak, and is close to the minimum between the $5f_{5/2}$ and $5f_{7/2}$ peaks. The $5f_{5/2}$ and $5f_{7/2}$ bands are fairly well separated with partial mixing. The $5f_{7/2}$ peak is centered at ~ 1.0 eV above the Fermi level, and only a small part of this band is occupied. Unlike the $5f$ electron configuration of atomic plutonium where all the $5f_{5/2}$ states are occupied and the

$5f_{7/2}$ states are empty, there are in the film case about four electrons in the $5f_{5/2}$ band and about one electron in the $5f_{7/2}$ band. Similar results were also found in a fully relativistic self-consistent bulk calculation (Brooks, Ref. 8). The center layer of $5f_{5/2}$ -to- $5f_{7/2}$ peak-peak splitting is ~ 1.3 eV which agrees with the fully relativistic scattering calculation.¹³ Here we also notice that the narrowing of the surface states is much more pronounced in the $5f_{5/2}$ band as compared to the $5f_{7/2}$ band. The surface-to-bulk ratio of the bandwidth of the $5f_{5/2}$ band is actually 0.70, which is much lower than our simple scaling with the coordination number estimate above. The reason for this is that the relativistic structure constants (in a κ, j notation) of the $5f_{5/2}$ band are exactly zero (Brooks, Ref. 8). This means that the bandwidth of the $5f_{5/2}$ subband is entirely associated with hybridization effects. (In a κ, j notation, this means that the $5f_{5/2}$ states hybridize also with the $5f_{7/2}$ states.) Accordingly this particular state is much more sensitive to the chemical surrounding, as is clear from Fig. 2, and scaling the bandwidths with the number of nearest neighbors breaks down.

The *ABCBA* stacking geometry used here probably does not significantly affect the result; LMTO bulk fcc and hcp calculations of plutonium we have performed give almost identical DOS and spin-orbit splitting. (The bulk calculations were performed using a LMTO code without atomic-sphere approximation supplied by David L. Price.)

B. Electronic structure of the (100) surface

The calculation of the electronic structure of the (100) surface was initiated by a self-consistent calculation with the $5f$ states in the core. The orbital charge densities from this calculation are listed in Table I, and the work function for this calculation was 3.5 eV.

We then calculated the scalar relativistic density of states (not shown) for the (100) surface, with the $5f$ states treated as bands. This calculation gave an atom-projected density of states of the central layer which is very similar to that of the (111) calculation and has the same width, 1.05 eV. However, the $5f$ surface states are much narrower than for the (111) calculation (0.82 eV), a fact that reflects the lower coordination number. Actually this bandwidth also scales approximately with the square root of the number of nearest neighbors, i.e., surface-to-bulk ratio of $\sqrt{8/12} \sim 0.82$ for the (100) orientation. In Fig. 3 we display the density of states from the fully relativistic calculation. Just as in the (111) calculation we find that the spin-orbit splitting is about 1.3 eV, and that the Fermi level lies in the valley between the $5f_{5/2}$ and $5f_{7/2}$ bands. Here the overall $5f$ surface density of states is also slightly narrower than for the bulk with the $5f_{5/2}$ subband again being much narrower than the $5f_{7/2}$ subband.

The orbital-projected charge densities for the (100) calculation are given in Table I, and it is found that the center layer shows occupation numbers in close agreement with those obtained from the (111) calculation,

TABLE I. Integrated charges (number of electrons) contained within spheres, resolved into orbital components. The radius of the muffin-tin sphere was 3.098 a.u. for all calculations.

Orbital charges	Without spin-orbit splitting				With spin-orbit splitting			
	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
(111) orientation								
5 <i>f</i> 's itinerant								
Center	0.450	0.150	1.378	5.056	0.446	0.150	1.353	5.076
Subsurface	0.454	0.149	1.387	5.008	0.447	0.143	1.360	5.031
Surface	0.412	0.124	1.224	5.025	0.424	0.123	1.216	5.040
Interstitial charge ^a			4.996				4.982	
Vacuum charge			0.404				0.425	
(100) orientation								
5 <i>f</i> 's localized								
Center	0.464	0.174	1.538					
Subsurface	0.436	0.167	1.520					
Surface	0.354	0.114	1.333					
Interstitial charge ^a			4.648					
Vacuum charge			0.328					
(100) orientation								
5 <i>f</i> 's itinerant								
Center	0.441	0.128	1.355	5.088	0.438	0.127	1.348	5.093
Subsurface	0.441	0.131	1.355	5.047	0.458	0.130	1.348	5.053
Surface	0.376	0.092	1.113	5.093	0.381	0.092	1.109	5.099
Interstitial charge ^a			5.377				5.342	
Vacuum charge			0.315				0.312	

^aThis is the interstitial charge per five-atom unit cell.

however the surface layer shows some difference, especially in the *d*-occupation number. This is a reflection of the difference in packing; the (111) surface is close packed whereas the (100) surface is more open.

The results presented above show that the ratio between the calculated scalar relativistic bandwidth of the surface layer and the bandwidth of the bulklike central layer scales approximately as the square root of the coordination number. To investigate this further we have also performed a calculation of a single-layer (100)-oriented slab (coordination number 6). The width of the 5*f* partial density of states from this scalar relativistic calculation is ~ 0.69 eV. This is in good agreement with the estimate obtained by scaling the “bulk” bandwidth of the (100) calculation with the square root of the coordination number $\sim 1.05\sqrt{6/12}=0.74$ eV. In Fig. 4 we show the DOS from a monolayer calculation which included the spin-orbit coupling. Here we see that just as in the five-layer (111) and (100) calculations the Fermi level is located in the valley between the 5*f*_{5/2} and 5*f*_{7/2} bands. Furthermore the 5*f*_{5/2} bandwidth here is only 0.3 eV.

The results presented above [both (111) as well as (100) orientation] suggest that for the scalar relativistic calculations the bandwidth scales with the square root of the coordination number. This implies that the 5*f* overlap is more important than hybridization effects. Treating the spin-orbit splitting, however, makes things more complicated. Analyzing the 5*f*_{5/2} and 5*f*_{7/2} subbands of the fully relativistic calculations shows that scaling the 5*f*_{5/2} subbands with the number of nearest neighbors does not

work. The reason is, as pointed out above, that for the 5*f*_{5/2} subband direct overlap effects are suppressed, and that the subband is more sensitive to hybridization effects.

C. Charge-density contour map

The charge-density contour map for the (111) surface is given in Fig. 5. This figure shows that the Pu atom has a large spherically symmetric charge distribution around each site. For the (100) surface we also show the charge-density contour map. Just as for the (111) surface, the charge density is more or less spherically symmetric around each site. The charge-density behavior for the (111) and (100) cases shown in Figs. 5 and 6 clearly shows behavior that is dominated by metallic bonding with evidence (provided by the slight “puckering” between spheres) for a small covalentlike contribution associated with hybridization.

D. Work function

The FLMTO method has provided reliable work-function values for various materials in previous calculations.³ In the present calculation we found a work function of 4.14 eV (3.68 eV) for the (111) [(100)] surface, with the 6*p* electrons treated as core states. For the 6*p* electrons treated as valence electrons, we obtain a much larger work function of 8.4 eV (with a widespread *p* band

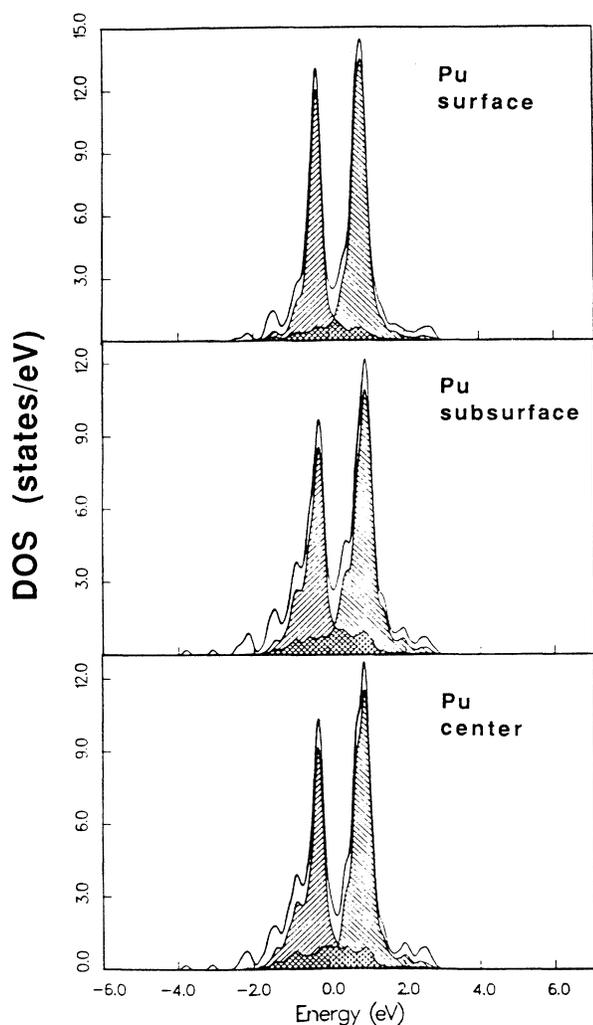


FIG. 3. Sphere-projected density of states from the (100)-relativistic calculation (with spin-orbit interaction). The area under the $5f_{5/2}$ partial density of states is hatched from left to right whereas the area under the $5f_{7/2}$ partial density of states is hatched from right to left. Energies are in eV and the Fermi energy is at zero.

present through the entire energy region treated, with features at 7–8 eV below the Fermi level). The work function with $6p$ electrons treated as core states compares quite favorably with experimental values for uranium¹⁴ (3.3–3.9 eV) (no experimental values are available for plutonium), indicating that treating the $6p$ electrons as localized is a good approximation.

Considering the core leakage for the $6p$ -in-core case (0.274 electron for the center atom), we feel that some further improvement of treating the $6p$ electrons is desirable. Since our results show that $6p$ electrons are almost localized, with a small degree of delocalization, an improvement would be to put them in semicore states and to use different energy windows to treat the $6p$ states and the true valence electrons.

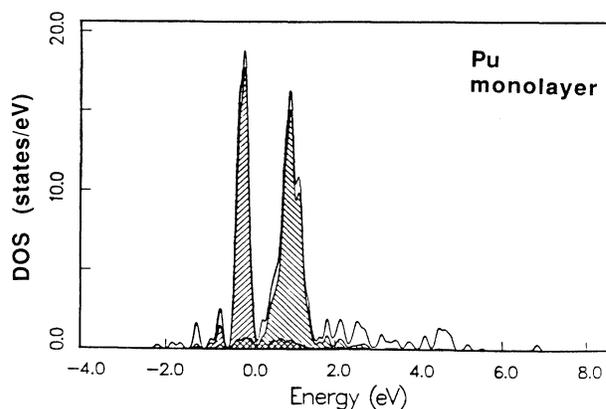


FIG. 4. Sphere-projected density of states from the (100)-relativistic monolayer calculation. The area under the $5f_{5/2}$ partial density of states is hatched from left to right whereas the area under the $5f_{7/2}$ partial density of states is hatched from right to left. Energies are in eV and the Fermi energy is at zero.

E. Conclusions

A key feature of the physics of the actinides is the nature of the $5f$ states, i.e., whether they are bonding or localized or how intermediate between these extremes. This is essentially determined by two competing effects,¹⁵ namely, the polarization energy obtained from Hund's rules for localized $5f$ states versus the bonding energy for itinerant $5f$ states. In the actinide metals the transition from localized-polarized to itinerant-bonding behavior for the $5f$ electrons is found to take place between Pu and Am.^{8,15} Because of lowered opportunity for overlap, the contribution to the bonding from $5f$ states is expected to be reduced at the surface as compared to the bulk.

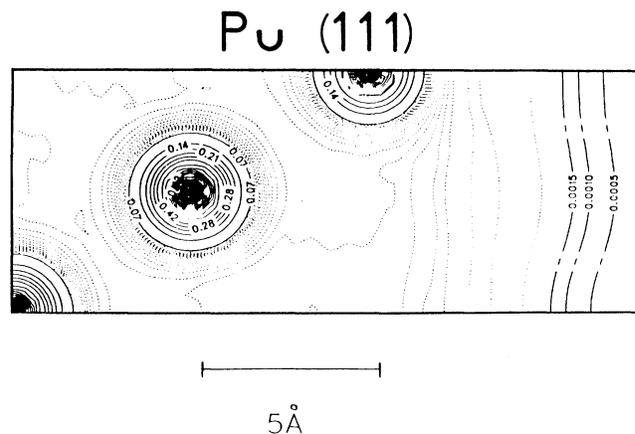


FIG. 5. Electron charge-density contour map (in units of electrons/a.u.³) for the (111) surface. The surface is at the right in the figure and the center of the slab is at the left. The cut is in the direction indicated in Fig. 1(a). The contours are plotted with three different spacings: 0.07 (solid line), 0.01 (dotted line), and 0.005 (dashed line).

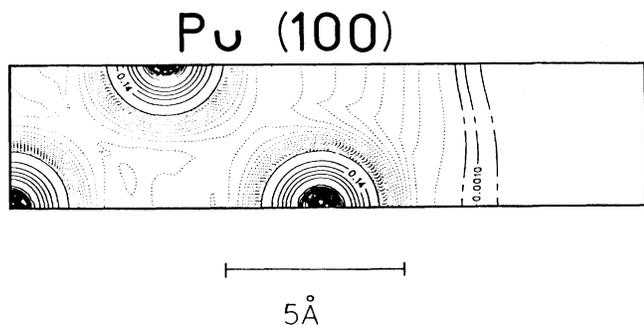


FIG. 6. Electron charge-density contour map (in units of electrons/a.u.³) for the (100) surface. The surface is at the right in the figure and the center of the slab is at the left. The cut is in the direction indicated in Fig. 1(b). The contours are plotted with three different spacings: 0.07 (solid line), 0.01 (dotted line), and 0.005 (dashed line).

Hence the polarized-localized $5f$ state of a surface atom might be favored over the itinerant, even though the bulk atoms are still itinerant. This would be an even more pronounced tendency for a single chemisorbed Pu layer that only weakly interacts with the substrate on which it has chemisorbed.

The results from the present calculation support this picture in the sense that we find that the $5f$ density of states is narrower at the surface than for the bulk, and the single-layer plutonium case gives the narrowest $5f$ density of states. The surface bandwidths are found to scale approximately as the square root of the coordination number (in the scalar relativistic calculations) and the band narrowing at the surface is therefore substantial. (In the $f_{5/2}$ case where only hybridization enters into the bandwidth, the surface narrowing is even more pronounced.)

For the (100) orientation we calculated the electronic structure for both localized and delocalized $5f$ states. The results obtained suggest that there is a small difference in the calculated work functions between the two approaches (3.5 versus 3.7 eV). The effect of $5f$ localization on the work function is also reflected in the anisotropy. The calculated work function is greater (4.1 eV) for the (111) surface having slightly more itinerant $5f$ electrons than for the (100) surface (3.7 eV). From this we suggest that the crossover from itinerant to localized surface states might be monitored by systematically studying the variation of the work function across the actinide series. Since we have found that δ -Pu shows a significant anisotropy in the work function depending on crystal orientation, we suggest that measurements of the surface electronic structure of metallic actinide materials

should preferably be made on single crystals.

The work function of a system is associated with the formation of a surface dipole moment.¹² This dipole moment emanates from the fact that some electrons “leak” out into the vacuum region. By examining the surface charge contours in Figs. 5 and 6, we can see that the charge leaks out further into the vacuum region for the (111) orientation. Also from Table I we notice that the (111) orientation has more charge in the vacuum region. Thus we can expect a larger surface dipole moment and a larger work function for the (111) orientation in agreement with the calculated behavior.

As discussed above in connection with Figs. 5 and 6 giving the charge density for the (111) and (100) cases, the present results indicate dominantly metallic bonding for δ -Pu with only a small covalentlike contribution associated with hybridization. In contrast to this behavior for the close-packed (fcc) δ -Pu structure, it is thought that covalent effects are important in giving the phases with open structures which occur among the lighter actinides. Thus an interesting question for possible future investigations is whether surface reconstruction effects occur for δ -Pu giving more open behavior with more pronounced covalency (hybridization). For instance, it might be that the atoms on the surface take a geometrical arrangement similar to those of another Pu allotrope (for example, α -Pu).

From the present calculation of the electronic structure of the plutonium surface, we have obtained interesting information about the behavior of the $5f$ electrons. A natural extension of this work is a calculation for uranium and other actinides, which would lead us to a better understanding of the overall trend of surface properties of $5f$ electron systems. As a matter of fact a study of (bcc) γ -uranium is planned for publication in the near future.¹⁶ Furthermore the present surface study provides us with a basis for investigating chemisorption of lighter atoms on actinide surfaces.

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