Possibility of a δ-like surface for α-Pu: Theory

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The electronic structure of a Pu square-mesh monolayer, a five-layer Pu (100)-orientation slab cut from a fcc lattice, and bulk fcc Pu have been calculated. For the monolayer calculation we allowed for spin and orbital polarization; and at all densities, from below the δ to above the α density, we found large spin and orbital moments. The equilibrium lattice constant for the monolayer was found to be expanded by about ~7%, compared to our bulk result (which is contracted ~7% from experiment). At both the theoretical and experimental α densities we found the five-layer slab to spin polarize, with spin moments close to that of the monolayer. Together with the experimental grazing-incidence photoemission, our results provide support for the existence of a small-moment δ-like surface state for the surface behavior of α plutonium.

I. INTRODUCTION

The physics and chemistry of actinide elements and compounds have been studied quite extensively during the past three or four decades.[1] The picture that has evolved for the elements is that the light actinides (Th-Pu) have delocalized $5f$ electrons which participate in the chemical bonding, and that from Am on, the $5f$ electrons are localized,[2–4] making the latter part of the actinide series similar to the rare-earth elements. Pu is therefore on the border between localized and itinerant f systems. The hypothesis that the early actinides have delocalized $5f$ electrons with a changeover to localized behavior at Am was supported by self-consistent spin-polarized energy band calculations (assuming a hypothetical fcc structure), which reproduced the overall trend in experimental volumes[4] as well as in the cohesive energies.[5,6] This pattern of behavior physically corresponds to a competition between $5f$ bonding and spin-polarization energies; this picture of a competition was tested by calculated modeling the effect of pressure on the degree of $5f$ electron localization in Am. Since the theoretical ground state of Am was found to be spin polarized with a completely occupied spin-up band and an empty spin-down band, the chemical bonding from the $5f$ electron is almost zero at atmospheric pressure.[4] However, the delocalization of $5f$ electrons in Am under pressure was demonstrated to occur and to be mainly determined by a competition between $5f$ bonding and (spin-) polarization energies.[3,4] In the present work we have studied the same physics, the competition between bonding and polarization energies, and have seen how this leads to $5f$-electron behavior for the surface and bulk of α-Pu.

It should be pointed out here that the approach used for Am, using delocalized basis states, to study the changeover between delocalized and localized f behavior is not as rigorous for Pu. For Am it was demonstrated that the trivalent $5f$ localized state could be well described using the same type of basis functions as for the earlier part of the series, i.e., a delocalized basis of

itinerant $5f$ electrons.[4] The reason why a delocalized basis describes a localized ground state so well for Am is that the number of $5f$ electrons can (almost) fill one spin f band leaving the other spin f band empty. A Bloch description of the (filled) spin-up f band is therefore equivalent to a localized Wannier orbital expansion.[7,4] However, for Pu, even if the f band polarizes completely, the spin-up f band will not be completely filled. This comes from the fact that the number of f electrons in Pu is ~ 5, whereas it takes 7 electrons completely to fill the spin-up f band. Nevertheless, it is interesting to see how a similar local spin-density approximation (LSDA) treatment describes the surface of α-Pu and bulk δ-Pu. (It should be pointed out here that the calculations that we will present for surface and bulk Pu do not rely on the atomic sphere approximation; see below.) In a bulk atomic sphere approximation (ASA) linear muffin-tin orbital (LMTO) calculation, Skriver, Johansson, and Andersen[4] and subsequently Solovyev *et al.*[8] found that δ-Pu spin polarizes, and that the spin moment is very large, $\sim 5\mu_B$. Moreover, the onset of spin polarization, and specifically complete polarization, is a strong indication of the system striving towards localization (e.g., the bulk calculation of γ-Ce, which has one localized $4f$ electron, gave a completely polarized $4f$ band, with one $4f$ electron in the spin-up band[9]). Since it has also been demonstrated that orbital polarization effects are important in narrow-band systems,[10] we will present calculations for a Pu monolayer that include both spin and orbital polarization.

Among the actinide elements (and perhaps also among the rest of the elements in the Periodic Table) Pu shows the most complicated crystal structure behavior. Pu has six stable allotropes. The low-temperature α phase is monoclinic (16 atoms per cell). However, small amounts of impurities (e.g., Ga) will stabilize the δ phase (fcc structure) at room temperature (the δ phase of pure Pu has a normal stability range of 320–450 °C). The experimental equilibrium volume (and bulk modulus as well as cohesive energy) of the α phase agrees more or less with what one would expect for delocalized $5f$ bands.[4–6,11] For instance, the equilibrium volumes of the light actinides, Ac to α-Pu, follow (roughly) a parabolic trend, indicating a chemically bonding $5f$ band (according to the Friedel model[12]). However, one should bear in mind that previous studies (assuming a hypothetical fcc structure)[4–6,11] show that, of the light actinides, energy-band calculations give the largest disagreement of the experimental equilibrium volume for α-Pu. A fact that we believe could be due to the complicated crystal structure found in α-Pu. The volume of the δ phase is substantially larger, and (at least at first sight) does not fit in with the picture of a delocalized f band. However, neither does the volume of δ-Pu correspond to a trivalent, localized $5f$ ground state, since it is substantially lower than the volume of trivalent Am. Instead, the volume of δ-Pu is somewhere between α-Pu and Am, possibly indicating that this phase of Pu is in the transition region between delocalized and localized $5f$ electron behavior. Thus we anticipate some difficulty in achieving a completely satisfactory description from a local-density approximation point of view.

This paper is largely motivated by some of our recent x-ray photoelectron spectroscopy (XPS) results,[13] and therefore, to provide background information, we will describe some earlier experimental and theoretical XPS efforts in the actinide metals. Since a delocalized $5f$ electron picture seems to describe the ground state well for the light actinides (Th to α-Pu), one would expect to see a strong XPS signal from these f states right at the Fermi level (E_F), with a width that corresponds to the band theoretical results. As an example that this is the case, we mention some recent experimental results by Cox[14] that relate to calculations by Albers *et al.*[15] on Np. In Np the experimental XPS spectra[14] show a strong signal at E_F, and the theoretical spectra roughly reproduces this experimental result, suggesting that the $5f$ bandwidth in this system is[15] ~ 3 eV. The same sort of agreement is seen in α-Pu.[16,13] In contrast to this, the experimental spectrum of δ-Pu is radically different.[13] The strong signal at E_F is shifted to higher binding energies, and the width of the signal is broadened to[13] 4–5 eV, in contrast to the calculated[17] density of states (DOS), which has the $5f$ band much narrower and pinned at E_F. This also indicates that the δ phase of Pu does not quite fit in the delocalized f-electron picture for the light actinides, and that the ground state of this phase is best described by not assuming delocalized $5f$ states. Most interestingly, this distinctly different behavior for δ-Pu compared to α-Pu allowed us to use recent XPS studies to indicate that the surface of α-Pu is δ-like.[13] By investigating the XPS signal for various degrees of grazing incidence we reasoned that the relative surface contribution to the total XPS signal could be modified. Specifically, it was found that at small grazing angles, where a larger portion of the surface should be probed, the XPS spectra became more δ-like. Similar effects have in fact been predicted[18] and confirmed experimentally[19] regarding the γ-like surface of α-Ce.

The present work is an attempt to give additional information, regarding the possibility of a δ phase being stable on the α-Pu surface.[13] We have therefore performed surface electronic structure calculations, based on the LSDA, for a monolayer of Pu. From these calculations we have extracted the equilibrium lattice constant of the Pu monolayer, and compared that to the calculated lattice constant of bulk Pu (assuming a hypothetical fcc structure). In addition, we have also performed calculations using a five-layer slab, similar to that previously done[20] for δ-Pu, but now allowing the possibility of polarization. In Sec. II we describe the details of the calculations, in Sec. III we present our results, and Sec. IV contains our conclusions.

II. DETAILS OF CALCULATIONS

The surface electronic structure has been calculated in the same way as described previously,[20,21] and we will only give a brief description here. We used the film-linearized muffin-tin orbitals method[21] for a monolayer, as well as for a five-layer slab, with a (100) orientation of a hypothetical fcc crystal. We used 16 muffin-tin orbit-

als[22,23] per atom and 22 plane-wave orbitals.[21] The warped potential was calculated according to Ref. 21, within the LSDA and with the parametrization of Vosko, Wilk, and Nusair.[24] The self-consistent, all-electron calculations were performed at various levels of approximation, e.g., both scalar relativistic (no spin-orbit coupling) and fully relativistic (with spin-orbit coupling included at each variational step[22,25]) calculations were made. The irreducible part of the two-dimensional Brillouin zone was sampled at ten "special k points"[26] in the five-layer calculation and 28 k points on a tetrahedral mesh for the monolayer calculation. In addition to allowing the surface calculations to spin polarize, we also included the orbital polarization with the procedure of Ref. 10. A $5f$ orbital was therefore shifted an amount $-E^3 L_\sigma m_l$ (for all other valence states these effects are very small[10]). Here E^3 is the Racah parameter for f states, m_l is the magnetic quantum number, and L_σ is the orbital moment from spin σ.

For the bulk calculations, we used a full-potential linear muffin-tin orbital technique.[27–29] These calculations were performed in the same way as has previously been described.[30] They were all electron, fully relativistic (spin-orbit coupling included at each variational step[22,25]), and employed no shape approximation to the charge density or potential. In these bulk calculations, integration over the Brillouin zone was done using special k point sampling.[31] The results reported here used 60 k points in the irreducible wedge of the fcc Brillouin zone.

III. RESULTS

We first present our results for the square-mesh monolayer calculations. The paramagnetic equilibrium lattice constant is shown in Table I together with the calculated bulk lattice constant. Notice that the monolayer exhibits a $\sim 4\%$ expansion of the lattice constant. This reflects the loss in $5f$ cohesion, which is associated with the narrowing of the $5f$ partial DOS at the surface. Notice in Fig. 1 that the DOS is dominated by the $5f$ contribution, and that $5f$ partial DOS is composed of two parts, the $5f_{5/2}$ and $5f_{7/2}$ partial DOS. The Fermi level (E_F) lies in the valley between these two peaks. The ratio between the $5f_{5/2}$ and the $5f_{7/2}$ occupation, R_2, has been pointed out as a measure of the importance of the spin-orbit splitting;[5] the larger R_2 ratio, the larger the influence of the spin-orbit splitting (for zero spin-orbit coupling this value is $\frac{6}{8}$, and for bulk Pu it is[5] ~ 2). We presently calculate this ratio to be ~ 6, and draw the conclusion that the influence of spin-orbit coupling is more important on the Pu surface than in the bulk, since the bandwidths are more narrow at the surface. As noted previously,[20] the bandwidth of Pu is quite heavily influenced by the spin-orbit coupling, which splits the $5f_{5/2}$ and $5f_{7/2}$ subbands apart by about 1.3 eV. It is therefore better to discuss band-narrowing effects for each subband separately, and as in our previous investigations[20] we find that, compared to the bulk[17] DOS, the $5f_{5/2}$ subband narrows more than the $5f_{7/2}$ subband (Fig. 1).

TABLE I. Theoretical lattice constants of the Pu monolayer and bulk Pu (a.u.). For the experimental α density the lattice constant of fcc Pu is ~ 8.1 a.u. and for the δ density it is ~ 8.8 a.u.

	Paramagnetic	Spin polarized	Spin and orbital polarized
Bulk	7.60		
Monolayer	7.93	8.10	8.13

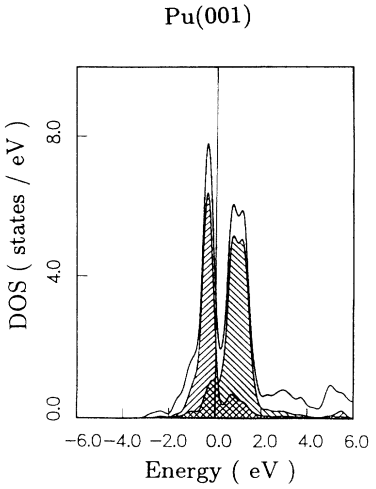

FIG. 1. DOS from the paramagnetic, fully relativistic monolayer calculation of Pu. The upper curve is the total DOS, whereas the hatched curves represent the $5f_{5/2}$ (hatched right to left) and the $5f_{7/2}$ (hatched left to right) DOS. Energies are in eV, E_F is at zero energy and is marked by a vertical line.

To investigate if polarization energies win over the band cohesion energies in determining the behavior, we then performed spin-polarized calculations. Since we find that a spin-polarized ground state has lower energy than the paramagnetic one, we conclude that LSDA predicts (spin-) polarization energies to be stronger than the band cohesion energies for the Pu monolayer. We found this to be the case for all lattice constants studied, and we show in Fig. 2 the calculated spin moments as a function of the lattice constant. The filled circles represent the total spin moment, whereas the open circles represent the $5f$ spin moment. For all volumes we find a substantial moment, which is dominated by the $5f$ contribution. From these calculations we get a $5f$ occupation very close to 5 (at the α density there are $0.08s$, $0.03p$, $0.86d$, and $5.13f$ electrons), and as is seen in Fig. 2, the $5f$ spin moment is close to $5\mu_B$, and therefore almost all $5f$ electrons are found in the spin-up band. The Pu slab therefore yields a result that is similar to the bulk δ-Pu and bulk Am results,[4] in the sense that the $5f$ band is exchange split so that the spin-up and -down $5f$ partial densities of states overlap very little in energy, and (almost) all $5f$ electrons are found in the spin-up band. There is an even further reduction in the $5f$ bonding associated with the spin polarization, since the lattice constant is increased relative to the paramagnetic calculations (Table I). This expansion is, of course, related to the presence of

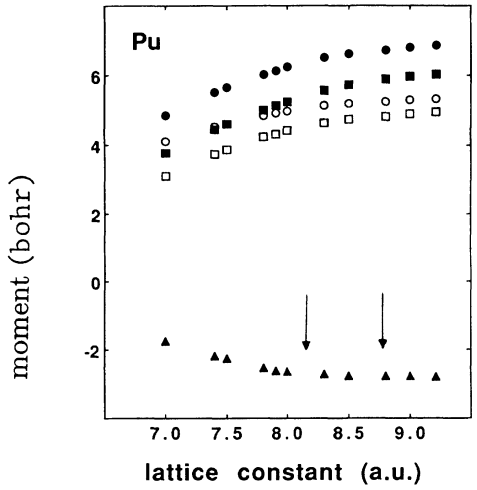

FIG. 2. Calculated spin and orbital moments for a Pu monolayer. The $5f$ spin moment is marked by an open circle for the scalar-relativistic calculation and by an open square for the fully relativistic, spin- and orbital polarization calculation. The total spin moment is marked by a filled circle for the scalar relativistic calculation and by a filled square for the fully relativistic, spin- and orbital polarization calculation. The orbital moment is marked by filled triangles. The lattice constant is given in atomic units. The lattice constant of α-Pu and δ-Pu are indicated by the two arrows.

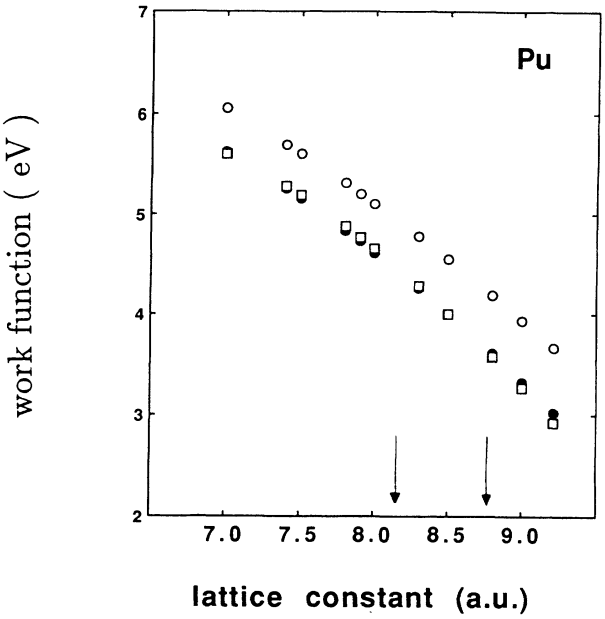

FIG. 3. Calculated work function (in eV) for a Pu monolayer. The results from the paramagnetic calculation are denoted by open circles, from the spin-polarized calculation by filled circles, and from the spin- and orbitally polarized calculation by open squares. The lattice constant is given in atomic units. The lattice constant of α-Pu and δ-Pu are indicated by the two arrows.

the polarization.

Finally we allowed for orbital polarization,[10] and we included the spin-orbit coupling at each variational step.[22,25] The spin and orbital moments so obtained are also shown in Fig. 2. The total spin moment is represented by filled squares, the $5f$ spin moment is represented by open squares, and the orbital moment by filled triangles. Since there is some mixing between spin-up and -down states when the spin-orbit coupling is included, the spin moment decreases slightly compared to the scalar relativistic results. Notice also that there is a substantial orbital moment, coupled antiparallel to the spin moment. This is in accord with Hund's third rule, stating the spin and orbital moments should be antiparallel for less than half-filled shell systems, and parallel for more than half-filled shell systems. The spin and orbital polarization calculation yields a slightly expanded lattice constant compared to the spin-polarized result, and the expansion compared to the calculated bulk data is ~7% (Table I). Notice from Fig. 2 that the spin (and orbital) moment is decreasing slowly with decreasing lattice constant, since the bands then become broader. Nevertheless, there are substantial spin and orbital moments even at the smallest lattice constant studied.

In Fig. 3 we show our calculated work functions from the monolayer calculations for the paramagnetic, the scalar relativistic spin polarized, and the fully relativistic, spin and orbital polarization calculations. Notice that for all three cases the work functions are increasing to values normally found in the transition metals (5±1 eV),[21] with decreasing lattice constant. Notice also that the onset of spin (and orbital) polarization changes the work function by a rather small amount, ~0.5 eV. We also point out that at a lattice constant corresponding to δ-Pu (~8.8 a.u.), the work function from the monolayer calculation is quite close to the value obtained from the five-layer calculation,[20] indicating that the monolayer results may represent the surface of an extended solid rather well.

The results discussed above indicate that the electronic behavior at the surface of α-Pu should not be described in the same way as bulk α-Pu, since (spin-) polarization energies are driving the monolayer to become spin (and orbitally) polarized, in contradiction to the experimental finding[1] of the absence of an ordered moment in α-Pu. However, it might be objected that a monolayer is never found in nature and that our calculations therefore do not describe the surface of α-Pu. We certainly feel that this is the weakest point of our calculations, and in order to investigate to what extent our monolayer describes the real α-Pu surface we have performed five-layer calculations in exactly the same way as previously,[20] but now including spin polarization. However, due to the complexity of the α-Pu structure, we are forced to assume a fcc structure (a common approximation[4]). The five-layer calculation was performed at two lattice constants, $a \approx 8.1$ a.u. (the experimental α-Pu volume) and $a \approx 7.6$ a.u. (the theoretical α-Pu volume[4,11]). The reason we did the five-layer calculation at two lattice constants is that it is known that the local spin-density approximation (assum-

ing a fcc structure and using ASA LMTO calculations) overestimates the spin-polarization energies in Pu, and that at the experimental lattice constant (ASA LMTO) LSDA yields[4] a spin moment of $\sim 2\mu_B$. However, at the theoretical lattice constant (ASA LMTO) LSDA yields a nonmagnetic ground state,[4] in agreement with experiment.

In Fig. 4 we show our calculated DOS from the paramagnetic, fully relativistic five-layer calculation with a lattice constant corresponding to the α density. Notice that the DOS looks very similar to our previous results[20] on δ-Pu, although the $5f$ bandwidth is broader. Furthermore, the bulk projected bandwidth agrees well with the data from our bulk fcc calculation at the α density, whereas the surface bandwidth is slightly narrower on comparing the full width at half maximum. Notice also that the bandwidth of the surface layer is broader than in the monolayer calculation (Fig. 1). Despite this there are similarities between the surface projected DOS of the five-layer calculation and the DOS of the monolayer calculation, e.g., the $5f$ partial DOS is composed of two parts, the $5f_{5/2}$ and $5f_{7/2}$ partial DOS < and the Fermi level (E_F) lies in the valley between these two peaks. The R_2 value for the surface projected DOS is also quite similar to the monolayer value, ~ 6.

One way to calculate the bandwidth is to evaluate the second moment of a partial DOS. The width of this partial DOS is then proportional to the square root of the second moment.[22] By calculating the bandwidth using this approach we find that both the $5f_{5/2}$ and $5f_{7/2}$ partial DOS are $\sim 20\%$ narrower at the surface. This is a more enhanced narrowing effect than what one gets from comparing the full width at half maximum, since in this second moment approach one also includes narrowing effects of the "hybridization tails." The above result is somewhat different from our study of the surface electronic structure of δ-Pu as well as from the monolayer calculation, where the $5f_{5/2}$ partial DOS showed a stronger narrowing at the surface compared to the $5f_{7/2}$ DOS. The work function for the slab calculation is 4.1 eV, and agrees fairly well with the results from the monolayer calculation, at this density. Moreover, the charge density contour from this calculation (Fig. 5) is also quite similar to our results for δ-Pu.[20] The charge density is spherically symmetric around each atom, and featureless in the interstitial. There is a slight "puckering" between the atoms, indicating that the bonding has some covalent character (although it is mostly metallic). The orbitally projected occupation numbers from this calculation are listed in Table II. Notice that the Pu slab has approximately five $5f$ electrons both in the bulk and at the surface. These occupation numbers are qualitatively the same as in our previous report on δ-Pu,[20] as well as our present results for the monolayer.

We now turn to the most interesting question, whether the surface states of the five-layer slab spin polarize in the same way that those in the monolayer calculation did. As seen in Table III, where we list our calculated spin moments, this is indeed the case and the spin moment of the surface layer is very close to the spin moment obtained from the monolayer calculation. The system is furthermore found to couple the spins antiferromagnetically between layers, and the spin moment is decreasing for the lower lying layers. However, in disagreement with experiment we do not find the center layer (bulk) to have zero spin moment, but in fact has a moment almost as large as that found in the bulk ASA LMTO calculation.[4] The DOS of our scalar-relativistic spin-polarized calculation is shown in Fig. 6. The antiferromagnetic coupling between the different layers is demonstrated here, and due to a large exchange splitting there is very little overlap in energy between the spin-up and -down bands. As seen in Tables II and III, there are approximately five $5f$ electrons for both bulk and surface Pu, and almost all of these $5f$ electrons occupy one spin channel, leaving the other empty. This behavior is very similar to the monolayer calculation. The spin density obtained from the above mentioned calculation is displayed in Fig. 7. Notice that the spin density is localized around the

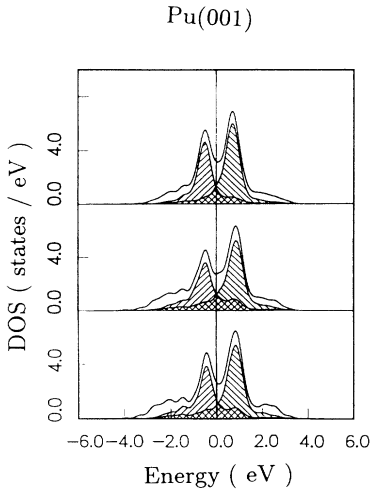

FIG. 4. DOS from the paramagnetic, fully relativistic five-layer slab calculation of Pu. The lowest panel represents the DOS projected to the center (bulk) layer, the middle panel represents the DOS projected to the subsurface layer, and the upper panel represents the DOS projected to the surface layer. The upper curve, in each panel, is the total DOS, whereas the hatched curves represents the $5f_{5/2}$ (hatched right to left) and the $5f_{7/2}$ (hatched left to right) DOS. Energies are in eV, E_F is at zero energy and is marked by a vertical line.

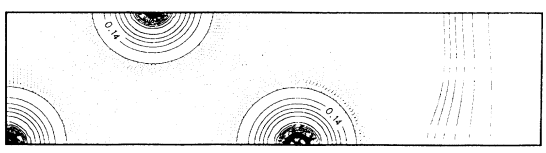

FIG. 5. Charge-density contour (in units of electrons/a.u.^{3}) from the paramagnetic, fully relativistic five-layer slab calculation of Pu. The surface is to the right in the figure. The cut is in the (100) plane. The contours are plotted with three different spacings: 0.07, solid line; 0.003, dotted line; and 0.0003, dashed line.

TABLE II. Occupation numbers $n(l)$, $l=s,p,d$, and f, from (a) relativistic (with spin-orbit coupling) paramagnetic Pu, (b) scalar-relativistic (without spin-orbit splitting) paramagnetic Pu, and (c) spin-polarized scalar-relativistic Pu. S denotes the surface layer, $S-1$ the subsurface-layer, and C the center (bulk) layer.

	$n(s)$	$n(p)$	$n(d)$	$n(f)$
		(a)		
C	0.368	0.117	1.406	5.048
$S-1$	0.370	0.109	1.395	5.039
S	0.328	0.093	1.100	5.148
n(interstitial/five atoms)=5.581				
n(vacuum)=0.306				
		(b)		
C	0.371	0.112	1.440	4.997
$S-1$	0.372	0.108	1.453	4.978
S	0.306	0.083	1.160	5.000
n(interstitial/five atoms)=5.907				
n(vacuum)=0.245				
		(c)		
C	0.347	0.110	1.338	5.216
$S-1$	0.359	0.098	1.384	5.199
S	0.272	0.079	1.022	5.287
n(interstitial/five atoms)=5.377				
n(vacuum)=0.210				

different atoms, and that it is spherically symmetric. This comes from the fact that the spin moment is dominated by the $5f$ orbitals, which are localized quite well around each atomic site.

Despite the fact that our calculations do not rely on the atomic sphere approximation, we predict that the center layer of the Pu slab (bulk) is magnetic, in disagreement with experiment. This could either reflect that our slab was not thick enough or that we encounter a shortcoming of LSDA in describing the ground state of Pu, assuming a fcc crystal. However, Skriver, Johansson, and Andersen[4] found that at *the theoretical equilibrium volume* Pu was paramagnetic. We therefore performed the same type of calculations at this density and found that the surface layer, as well as the other layers, spin polarized. The coupling here is also antiferromagnetic, although with slightly smaller spin moments than for the α density (see Table III). We believe that the failure to describe the bulk layer properly (experiments indicate bulk δ-Pu should have no spin moment) is a reflection of the surface moment inducing a magnetic moment in the lower-lying layers, and that one needs a very thick slab to get a nonmagnetic bulk layer[32,33] (the $5f$ spin moment drops only by $0.1\mu_B$ between the subsurface and bulk layer). Presumably a very thick slab would yield a nonmagnetic bulk behavior, whereas at the surface a moment

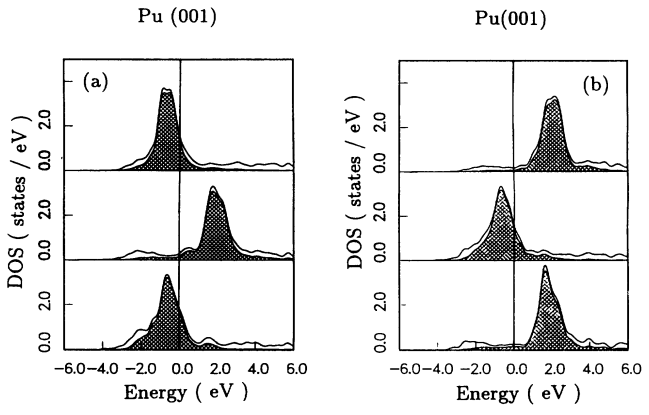

FIG. 6. DOS from the spin-polarized, scalar-relativistic five-layer slab calculation of Pu. The spin-up DOS is plotted to the left (a) and the spin-down DOS to the right (b). The lowest panel represents the DOS projected to the center (bulk) layer, the middle panel represents the DOS projected to the subsurface layer, and the upper panel represents the DOS projected to the surface layer. The upper curve, in each panel, is the total DOS, whereas the cross-hatched curves represents the $5f$ DOS. Energies are in eV, E_F is at zero energy and is marked by a vertical line.

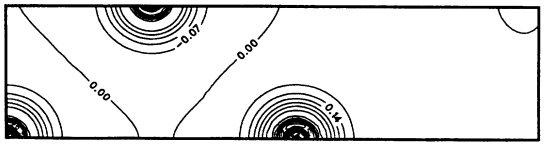

FIG. 7. Spin-density contour (in units of bohr/a.u.^{3}) from the spin-polarized, scalar-relativistic five-layer slab calculation of Pu. The surface is to the right in the figure. The cut is in the (100) plane. The contours are plotted with a 0.07 spacing.

TABLE III. Magnetic moments $m(l), l=s,p,d$, and f, from spin-polarized scalar-relativistic Pu at two densities, $a=8.1$ and $a=7.6$. S denotes the surface layer, $S-1$ the subsurface layer, and C the center (bulk) layer.

	$m(s)$	$m(p)$	$m(d)$	$m(f)$
		$a=8.1$		
C	0.011	−0.006	0.186	4.434
$S-1$	−0.023	0.002	−0.228	−4.529
S	0.022	0.001	0.244	4.921
		$a=7.6$		
C	0.004	−0.010	0.174	3.539
$S-1$	−0.013	0.001	−0.185	−3.646
S	0.020	0.001	0.225	4.357

would still be present (but smaller than our calculated one).

IV. CONCLUSION

It seems that although the interaction with the lower-lying Pu layers broadens the surface DOS of the five-layer slab, compared to the monolayer, there are many similarities; e.g., the $5f$ occupation, the spin moment, the general shape of the DOS, the R_2 value, and even the work function, which for the spin-polarized α density slab was 4.3 eV (cf. Fig. 3, the paramagnetic work function was 4.1 eV). This we believe provides some argument that the monolayer describes reasonably well the surface state of Pu. It then seems that LSDA describes bulk δ-Pu (Ref. 4) and the surface of Pu (at the α density and higher densities) in a very similar way. Namely, polarization energies are overcoming almost all $5f$ bonding, resulting in an expanded lattice constant. It is interesting to observe that our monolayer calculation is expanded by approximately the same amount as bulk δ-Pu when compared to the α phase. Our results from the five-layer slab calculations suggests that a very thick slab is necessary to obtain bulk behavior for the center layer. With increasing thickness of the slab, we expect not only the bulk moment to decrease (to zero), but also the surface moment to decrease. However, we believe that the present calculations give evidence of a magnetically ordered surface of α-Pu. It is at present outside the scope of this investigation to perform a very thick slab calculation, since these calculations would be extremely large.

The results presented above give evidence that the surface electronic structure of α-Pu is similar to the electronic structure in the δ phase. Namely, using the same way of describing the electronic structure (band structure techniques based on the LSDA), it is very hard to notice any difference between the surface of α-Pu and bulk δ-Pu. These results, together with the available XPS data,[13] suggest the possibility of α-Pu having a δ-like surface layer.

Finally, there is a possible new and significant surface magnetism effect that may occur in Pu because of the large predicted surface *orbital* moment. This is the possibility of a marked anisotropy in the ordered moment. We have assumed a moment normal to the surface [i.e., along (001)]. A moment in any other direction would lower the symmetry, and the moment could differ significantly. For such an investigation a different k mesh, reflecting the lowered symmetry, should be used.

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