On the electronic configuration in Pu: spectroscopy and theory

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Abstract
Photoelectron spectroscopy, synchrotron-radiation-based x-ray absorption, electron energy loss
spectroscopy, and density-functional calculations within the mixed-level and magnetic models,
together with canonical band theory, have been used to study the electron configuration in Pu.
These methods suggest a $5f^n$ occupation for Pu of $5 \leqslant n < 6$, with $n \neq 6$, contrary to what has
recently been suggested in several publications. We show that the $n = 6$ picture is inconsistent
with the usual interpretation of photoemission, x-ray absorption, and electron energy loss
spectra. Instead, these spectra support the traditional conjecture of a $5f^5$ occupation in Pu as is
obtained by density-functional theory. We further argue, based on 5f-band filling, that an $n = 6$
hypothesis is incompatible with the position of Pu in the actinide series and its monoclinic
ground-state phase.

(Some figures in this article are in colour only in the electronic version)

The combined efforts of experiment and theory have promoted considerably the understanding of the actinides during recent years. For instance, diamond-anvil-cell studies of pressure-induced phase transitions in the actinides are well accounted for by density-functional theory (DFT) and explained by the broadening of 5f bands, that then become less able to sustain the distorted geometries displayed in the more 5f-bonded metals such as U, Np, and Pu metals [1]. Although phase instabilities are direct consequences of the narrow 5f-band electronic structure, the electronic and magnetic structures of plutonium, in particular, are still being debated [2–10] and not fully understood. It is important to clarify the situation because only from this understanding can a consistent picture for plutonium emerge. The unusual properties of Pu are well documented and include, but are not limited to, its complex phase diagram having many high-and low-symmetry phases, with large volume changes associated with the phase transitions, and a combination of large positive (α, β, and γ) and negative (δ and δ') thermal expansions [11].

Recent experiments aimed at illuminating the electronic structure include photoemission [12], x-ray absorption and electron energy loss [13], magnetic susceptibility [14], and heat capacity [15]. Theoretically, DFT that allows for formation of spin and orbital moments [6, 16] appears to accurately determine total energies as well as some, but not all, aspects of the electronic structure of the known phases of Pu, with one particular problem being the failure of the DFT approach to reconstruct the experimental observation of the zero magnetic moment for δ-Pu. The mixed-level model [2] is able to reproduce the photoemission spectra of Pu in detail within a completely 'non-magnetic' model, but has for now been restricted to the δ phase and artificially separates localized and delocalized 5f states. An approach founded on the dynamical mean-field theory (DMFT) [4] has also been applied to the δ phase, although the interpretation by this work is unclear and has changed over time [5]. Until recently, the valence-electron configuration of Pu has not been questioned in either of the aforementioned experiments or models, but the around-mean-field (AMF) LSDA + U theory [8] suggests an americium-like, non-magnetic ($J = 0$) $5f^6$ configuration

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for Pu. Independently, an LDA $+ U +$ SO (spin–orbit interaction) approach was pursued by Shorikov *et al* [9], who arrived at this same conclusion. By itself, as mentioned by the authors [8], this model does not reproduce the known photoemission spectra due to the formation of a pseudo-gap at the Fermi level, a recognized problem with the LSDA $+ U$ approach [3]. This deficiency was, however, addressed in an improved scheme that includes dynamical electron correlations (AMF–DMFT) [10].

In this paper we investigate the possibility of a $5f^6$ bonding configuration for Pu by means of photoemission, x-ray absorption, electron energy loss spectroscopy, and electronic structure theory.

1. X-ray absorption and electron energy loss spectroscopy

The data from x-ray absorption (XAS) and electron energy loss spectroscopy (EELS) indicate that the number of 5f electrons, n, involved in bonding of Pu must be at least as great as five and less than six. The equivalence of the XAS and high-energy EELS measurements for assessing the electronic states has already been demonstrated for Ce and Pu, as well as for other actinides [13, 17–19]. The argument against $n = 6$ will now be discussed in a step-wise fashion.

1.1. The relative diminishment of the Pu $4d_{3/2}$ peaks indicates strong relativistic effects in the Pu 5f states, i.e. a jj-coupling or jj-skewed intermediate coupling scheme

As can be seen in figure 1, the intensity of the $4d_{3/2}$ peak of Pu is significantly reduced versus that for U [20]. This large reduction is driven by the combination of the electric dipole selection rule that forbids the transition from a pure $d_{3/2}$ peak into a pure $f_{7/2}$ peak and the preferential filling of the $5f_{5/2}$ dominated sublevel. The reduction also implies that the Pu 5f states must be split into two lobes, the lower (mainly occupied) lobe being principally pure 5/2 character and the upper (unoccupied) lobe being principally pure 7/2 character. This picture is shown schematically in figure 2. The result is independent of any particular theoretical model for spin–orbit splitting or the calculation of x-ray absorption cross section and thus does *not* depend upon the details of the branching ratio analysis presented previously [12, 18].

While the results in figure 2 may seem trivial, they are in fact exceptionally important. Despite the occasional attempts at the inclusion of relativistic effects [21], amongst some parts of the scientific community non-relativistic calculations of Pu electronic structure were the norm and defended vigorously. The irrefutable experimental demonstration of the relativistic nature of the Pu 5f states is crucially important and the underlying basis of the XAS/EELS analysis.

1.2. Coupled with the result in section 1 above, the absence of a pre-peak in the Pu 5d XAS and EELS indicates that n must be at least 5.

As shown in figure 3, there is a pre-peak in the EELS 5d to 5f transition for Th and U, but not for Pu. Similar results (figure 4)
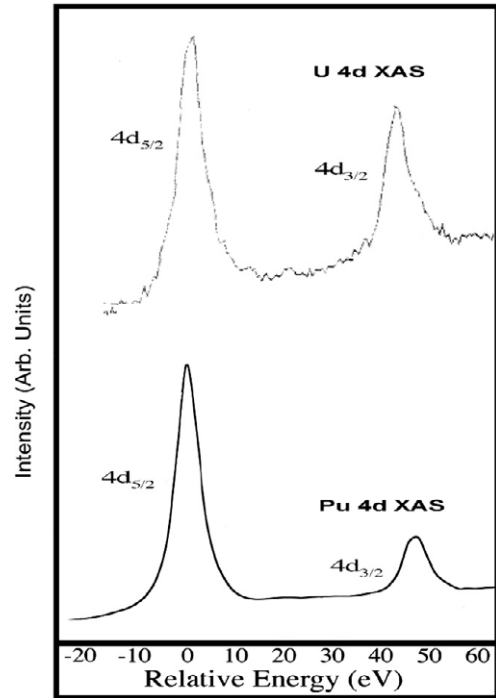

Figure 1. The 4d to 5f XAS transition results for Pu [13] and U [20] are shown here. The photon energies are near 800 eV.

have been obtained for 5d XAS [17]. The pre-peak structure in the 4d XAS of the rare earths was explained many years ago by Dehmer *et al* [22]: it is driven by the combination of angular momentum coupling between the 4d and 4f states and the dependence of the Coulombic energy term upon the coupling details. The spectroscopic transition for the rare earths can be summarized as follows.

$$4d^{10}4f^n + h\nu \rightarrow 4d^9 4f^{n+1}. \tag{1}$$

When $n = 14$, there is no transition. When $n = 13$, there is a single main peak, without any pre-peaks [17]. This is because partial occupation of both the d and f states is required for coupling. If $n = 13$ and $n + 1 = 14$, then in the final state the 4f level is filled and no coupling occurs. For the lighter actinides ($n < 6$), the situation is similar but not identical.

$5d_{5/2}$, pure jj, $n < 6$
$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^n(5f_{7/2})^0 + h\nu$$
$$\rightarrow (5d_{3/2})^4(5d_{5/2})^5(5f_{5/2})^{n+1}(5f_{7/2})^0$$
$$+ (5d_{3/2})^4(5d_{5/2})^5(5f_{5/2})^n(5f_{7/2})^1 \tag{2}$$

$5d_{3/2}$, pure jj, $n < 6$
$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^n(5f_{7/2})^0 + h\nu$$
$$\rightarrow (5d_{3/2})^3(5d_{5/2})^6(5f_{5/2})^{n+1}(5f_{7/2})^0. \tag{3}$$

Again, transitions from $d_{3/2}$ to $f_{7/2}$ are forbidden. For the pre-peaks at lower $h\nu$, we need only consider the $(5f_{5/2})^{n+1}$ terms. (Transitions into the $f_{7/2}$ states will generally need higher energies and pre-peaks that might be associated with this transition will be coincident with the main $f_{5/2}$ spectral structure and lost therein.) The final state 5/2 level will be
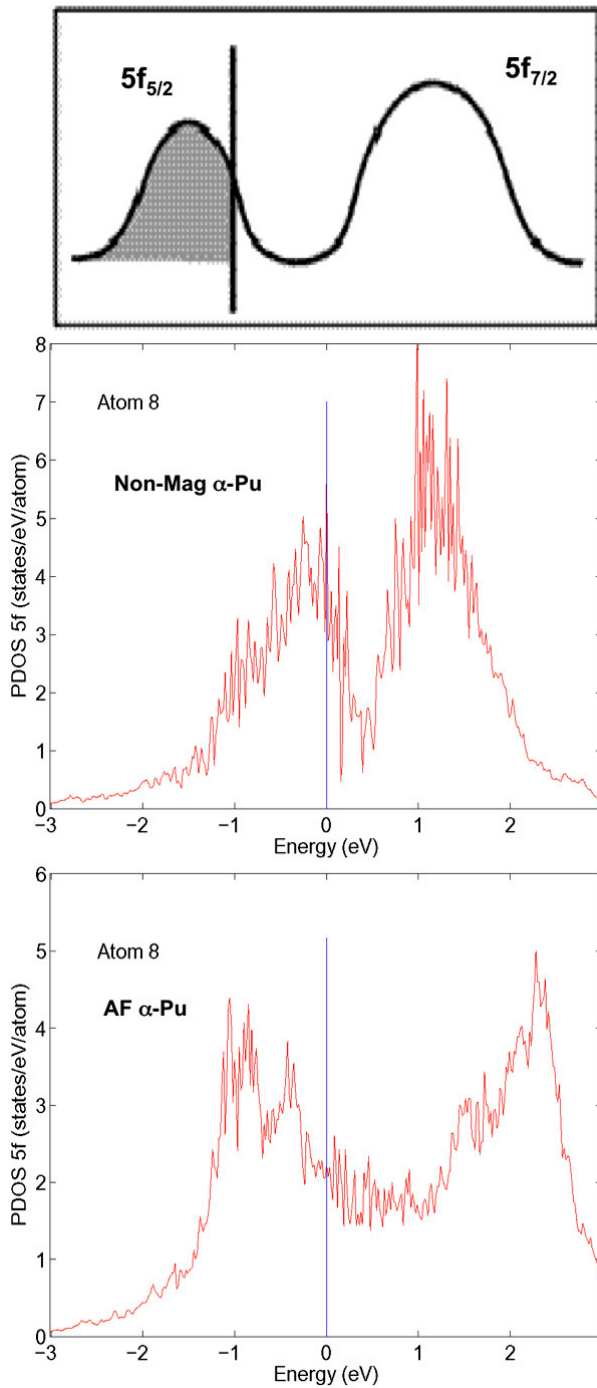
Figure 2. The two lobed structure of the Pu 5f density of states is shown here. Top: the simple picture derived from the spectroscopic analysis. Middle: the result of non-magnetic calculation by Kutepov, including the spin–orbit splitting in the Pu 5f states. Bottom: the result of an anti-ferromagnetic calculation by Kutepov, including the spin–orbit splitting in the Pu 5f states. The Fermi energy (0 eV) is shown by a vertical line, with occupied states to the left and unoccupied to the right. PDOS is partial density of states. See [13] for details concerning this figure.
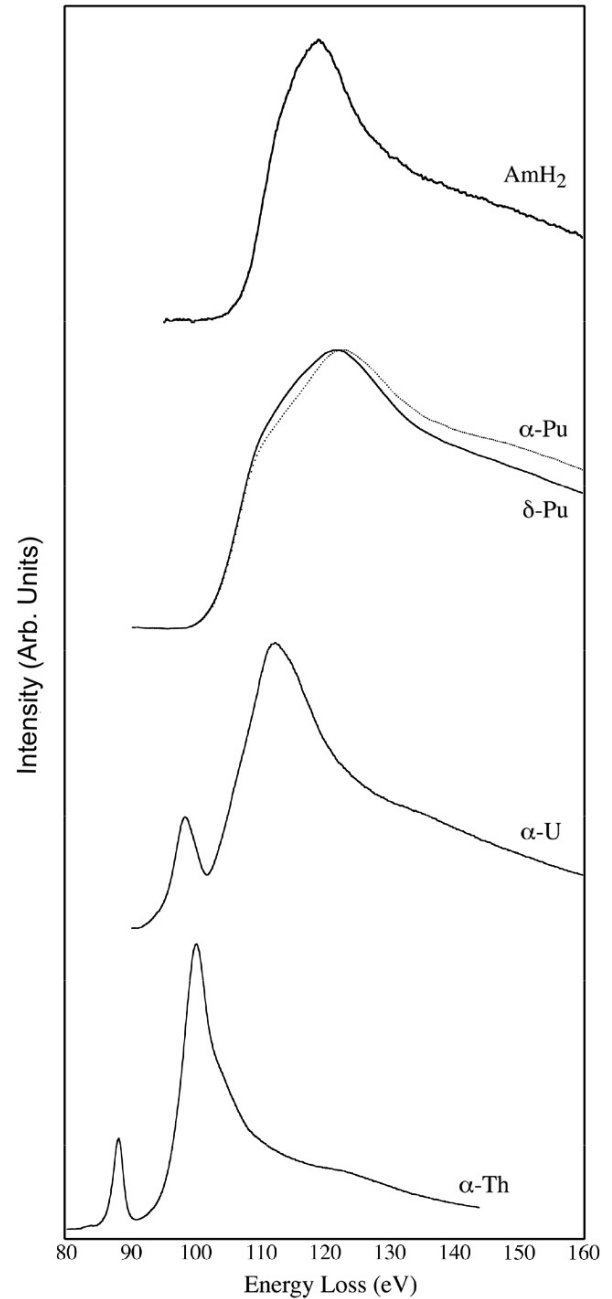

Figure 3. The EELS spectra of the 5d to 5f transitions of Th (bottom), U, (second from bottom), Pu (second from top), and AmH_2 (top) are shown here. The Th, U, and Pu data are from [17]. The AmH_2 data are from [23].

filled at $n + 1 = 6$ or $n = 5$. For $n < 5$ (e.g. Th and U), there will be pre-peaks. The absence of pre-peaks for Pu, both the α and the δ phases, indicates that n must be 5 or greater. This raises the question: what about an n of 6 and above for Pu? For $n \geqslant 6$, the transition looks like this.

$5d_{5/2}$, pure jj, $n \geqslant 6$

$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^6(5f_{7/2})^{n-6} + h\nu$$
$$\rightarrow (5d_{3/2})^4(5d_{5/2})^5(5f_{5/2})^6(5f_{7/2})^{n-5} \quad (4)$$

$5d_{3/2}$, pure jj, $n \geqslant 6$

$$(5d_{3/2})^4(5d_{5/2})^6(5f_{5/2})^6(5f_{7/2})^{n-6} + h\nu$$
$$\rightarrow \text{No transition allowed.} \quad (5)$$

Once again, there will be no transition in equation (5) because $d_{3/2}$ to $f_{7/2}$ transitions are forbidden.
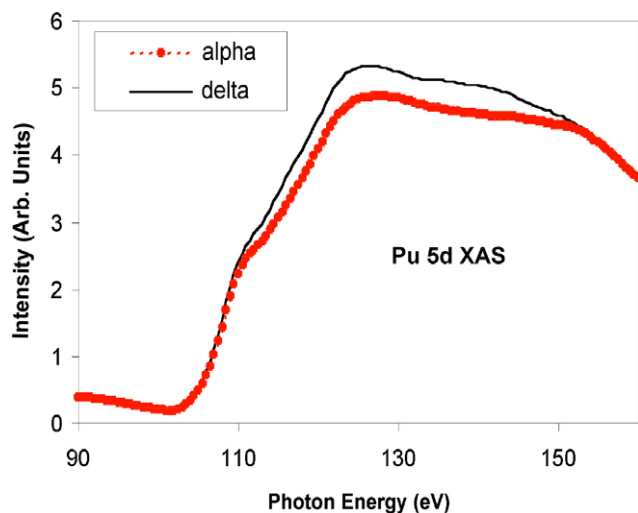
Figure 4. The XAS data for the 5d to 5f transition in Pu is shown here. The spectra are taken from [17].

Figure 5. The electron diffraction and EELS data for the 4d–5f transition of Am, from an AmH_2 sample, is shown here. The data are taken from [23].

Figure 6. The EELS data for the 4d to 5f transition in α'-Pu and δ-Pu are shown here. The spectra are taken from [23]. α'-Pu is shown in black (dark line) and δ-Pu is shown in blue (light line).

The situation is different in another, subtle way as well. A filled $5f_{5/2}$ level now stands between the partially occupied 5d and $5f_{7/2}$ levels. It is unclear whether angular momentum coupling (and thus pre-peak formation) will occur under these conditions. In fact, the spectrum from AmH_2 shown in figure 3 exhibits no evidence of pre-peaks. Although this is not a spectrum from an elemental actinide, past experiments have shown that for a given actinide the peak-ratio values tend to be grouped together, with larger separations between the elemental groups [23]. The grouping tended to be tightest for actinide elements that exhibited a strong localization even in the elemental, metallic state.

1.3. The presence of two edges in the Pu 5d XAS and a substantial peak in the $4d_{3/2}$ XAS indicate that $n < 6$

As can be seen in the 5d XAS of both α- and δ-Pu (figure 4), there are two strong edges for $h\nu = 110$–120 eV. A similar, albeit weaker, structure is observed in the EELS of α- and δ-Pu, as shown in figure 3. These two steps are the leading edges of the main $5d_{5/2}$ (about 110 eV) and $5d_{3/2}$ (about 120 eV) transitions. (Confirmation of the initiation of the 5d transition near 110 eV can be gleaned from photoelectron spectroscopy. In the wide photoemission scans shown in figures 3 and 6 in [24], there is a strong spectral feature at a binding energy of about 100 eV, assigned as the 5d manifold. See [24] and references therein.) As illustrated in equation (5), if $n = 6$ or more, one of the two transitions is lost. This is exactly what has happened in AmH_2, as shown in figure 3. Here, the second spin–orbit split peak is essentially gone, or at least strongly attenuated, and lost in the tail of the other peak/edge. The overall peak structure of the 'giant resonance' of AmH_2 is now about half as wide as that of Pu. Thus, the presence of two strong edges indicates that $n < 6$ for Pu.

An analogous process will occur for the 4d–5f transitions. For a pure jj-coupling scheme and electric dipole selection rules, the $4d_{3/2}$ peak should vanish. In reality, there will be mixing between the pure $5f_{5/2}$ and $5f_{7/2}$ states, so at $n = 6$ one
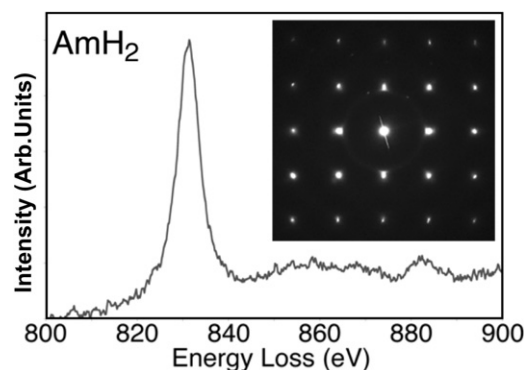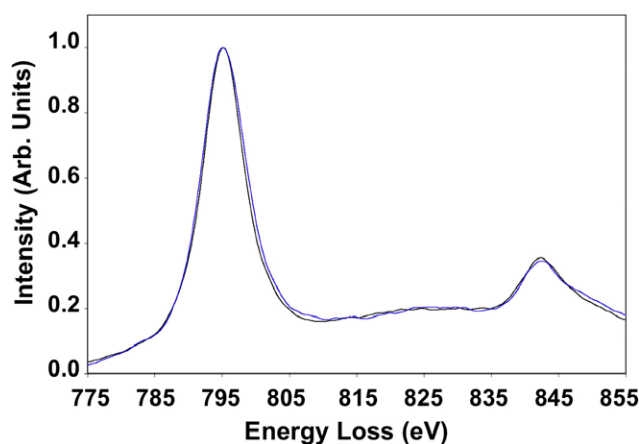
would expect a small but almost negligible $4d_{3/2}$ peak. Again, this is exactly what has been observed for AmH_2 as shown in figure 5 [23]. The Pu $4d_{3/2}$ peak is too large for $n = 6$, and therefore for Pu $n < 6$.

What about the possibilities for Am being $n > 6$? This seems unlikely. As will be discussed below, there is very strong evidence that Am has $n = 6$. Additionally, recent measurements on Cm [25] indicate that $n = 7$, within an LS-like coupling scheme. The return to an LS skewed intermediate case for the heavier actinides is consistent with the atomic model of van der Laan and Thole [26], which has been used to explain the cross-sectional behavior of the lighter actinides [13, 19].

Before going onto a discussion of photoelectron spectroscopy, it is useful to consider the possibility of phase specific variations of the XAS/EELS findings and thus the n value for Pu. As can be seen in figures 3 and 4, within each technique, the results for α and δ are quite similar for the 5d to 5f transitions. Additionally, as shown in figure 6, the $N_{4,5}$ electron energy loss spectra for α and δ Pu are again similar [23]. The experimental data hence point towards the conclusion that for Pu n is less than six and greater than or equal to five, for both the α and the δ phases. This does not rule out that there
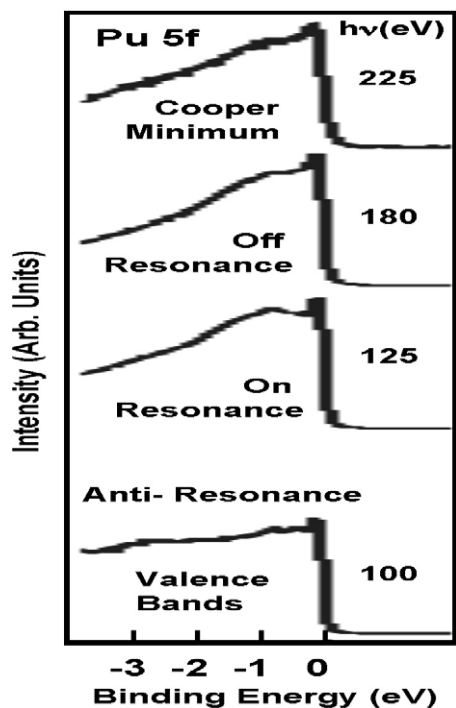
Figure 7. Shown here are photoelectron spectroscopy data for Pu at $h\nu = 225$, 180, 125, and 100 eV. The data are taken from [24]. The Fermi energy is at 0 eV. These data are from an α-Pu (bulk) sample with a δ-like surface reconstruction. They are nearly identical with data from a bulk δ-Pu sample [24].

may be phase specific variations between the spectra, but these are small compared to the variation from element to element.

Thus, to summarize for Pu 5f occupation: from XAS and EELS, $5 \leqslant n < 6$, with $n \neq 6$.

2. Valence band photoelectron spectroscopy (PES)

Photoelectron spectroscopy measures transitions between states, using an electron that is ejected from the material. If the measurements are angle resolved and the samples are single crystals, then one may glean information about the dispersion of specific states from the PES of the valence bands [27]. If the sample is polycrystalline or a significant angle averaging is applied, then one may get information about the initial density of states, as in electron spectroscopy for chemical analysis (ESCA), usually performed at high photon energies [28, 29]. In the case of Pu, invariably the samples are not single crystals and most of the high-energy-resolution valence band PES has been performed at low energies using He I (21.22 eV) or He II (40.8 eV) excitation sources [12, 30]. With Pu, there is a history of interpreting the spectral features in terms of multiplet structures [31, 32]. In ESCA of Pu with laboratory sources (e.g. with Mg Kα at $h\nu = 1254$ eV) the resolution is not sufficient to isolate the fine structure of interest in the valence bands [33]. However, there is one synchrotron-radiation-based study of Pu, which provides significant guidance concerning how to interpret the valence band PES of Pu [24].

(1) Other than intensity variations and a slight loss of fine structure with increasing energy, the valence band spectra
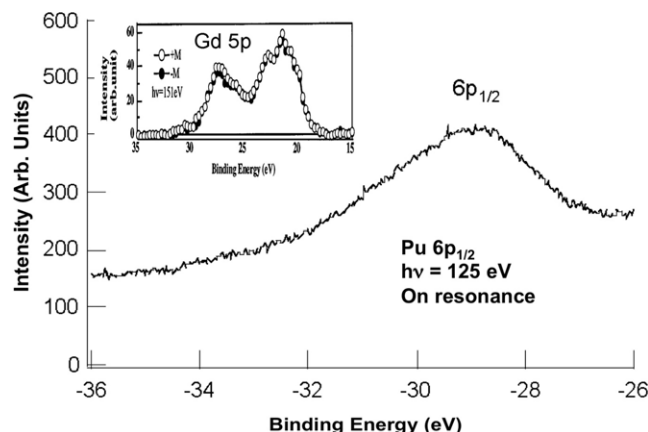

Figure 8. PES data of the Pu $6p_{1/2}$ peak are shown here, from the same sample as in figure 7, along the Gd 5p data in the inset [24]. Both correspond to being on resonance, i.e. at the same energy as the 4d to 4f resonance in Gd and the 5d to 5f resonance in Pu. For Gd, the photon energy is 151 eV and the $+$M and $-$M signify reversed remnant magnetizations. See [24] for more details. For more Gd data, please see [34].

of Pu are the same over a very wide photon energies, as shown in figure 7. The photon energies include $h\nu = 225$ eV (at the Cooper minimum), 180 eV (off-resonance), 125 eV (on-resonance), and 100 eV (at the anti-resonance) [24]. In all, the spectral structure is essentially the same: a peak near the Fermi level, followed by a minimum at a binding energy of $1/2$ eV and a broad maximum at about 1 eV. Qualitatively, these spectra suggest some underlying constancy to the PES response of δ-Pu and thus support the validity of the previous lower-energy studies using the He I and He II laboratory sources.

(2) There is no observable multiplet structure in the Pu $6p_{1/2}$ spectrum, unlike the Gd 5p spectrum [24, 34], as seen in figure 8. The Pu 6p feature is wider due to the increased lifetime broadening of the actinides relative to the rare earths, but, considering the size and energy separation of the Gd satellite peaks, if there were comparable structure in the Pu $6p_{1/2}$ spectrum, it would be observed. The absence of multiplet structure in the Pu $6p_{1/2}$ spectrum questions strongly the process of analyzing the valence bands of Pu within the usual multiplet structure approach [31, 32].

These two results taken together strongly suggest the following: the valence band spectra of δ-Pu may be representative of the electron density of states and should be compared directly to the predictions of electronic structure theory. While these two observations are not conclusive proof that the PES spectra are directly equivalent to the Pu DOS, there is nothing here to contraindicate the validity and utility of the process.

Again, it is important to bear in mind that photoelectron spectroscopy is a measure of the joint density of states, weighted by transition probabilities. However, the absence of a photon energy dependent variation (point (1) above) and the absence of a multiplet feature in the Pu $6p_{1/2}$ (point (2)
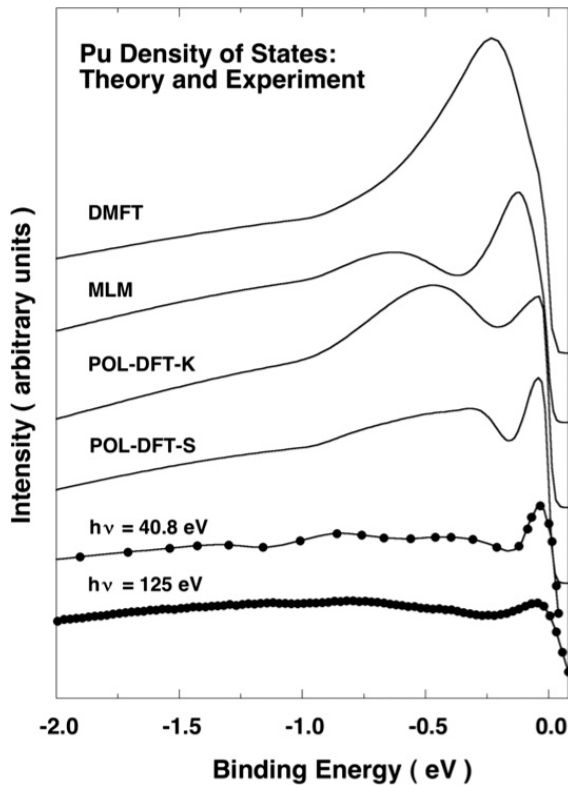
Figure 9. Present δ-Pu photoemission spectra ($h\nu = 125$ eV) and that of Arko *et al* at $h\nu = 40.8$ eV [12], compared with convoluted electronic density of states obtained from the mixed-level model (MLM) [2], polarized DFT (DFT-POL–Söderlind *et al* and DFT-POL–Kutepov and Kutepova) [6, 35], and around-mean-field dynamical mean-field theory (AMF–DMFT) [7]. Because of the increased instrumental broadening (about 0.1 eV) of the $h\nu = 125$ eV data, the Fermi edge and the peak near the Fermi edge (0.0 eV) are significantly broadened. Thus, while the synchrotron radiation results of figure 7 validate the higher resolution data taken at $h\nu = 40.8$ eV, the best comparison with experiment must be made with the resonance lamp spectrum at $h\nu = 40.8$ eV.

above), plus the historical precedence [28, 29], all point toward the utility of making this comparison. Thus, if only as an academic exercise, we will compare our spectra with theory to hopefully help distinguish between proposed models. In figure 9 we show our measured PES together with calculations of the convoluted DOS[6] by Eriksson *et al* [2], Söderlind *et al* [6], Pourovskii *et al* [10], and Kutepov and Kutepova [35]. The details of the calculations can be found in these references, whereas all convolutions were the same as in [6], but with a Gaussian broadening width of 3 mRyd instead of 6 mRyd for a better instrumental resolution. The first of these models is referred to as the mixed-level model (MLM), and assumes a $5f^5$ configuration for δ-Pu, that is divided into electrons with localized (four) and itinerant (one) character. The MLM does not allow formation of magnetic moments, whereas the second model, spin/orbital polarized DFT (POL-DFT) does, but still predicts a $5f^5$ Pu state. The latter is in many respects very similar to those by Kutepov and Kutepova [35], whose results confirmed $n \sim 5$. In contrast to these approaches, the more

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[6] DOS convoluted as described in [11].

recent models by Pourovskii *et al* [10] and Shorikov *et al* [9] dictate a non-magnetic $5f^6$ configuration of Pu.

Note in figure 9 that the $5f^5$-configuration models (MLM and POL-DFT) both capture the very narrow peak close to the Fermi level in close agreement to the measured spectra, but in complete disagreement with the AMF–DMFT result [10]. Also, the broad feature at ~ -0.25 eV in the AMF–DMFT does not correspond to PES, that instead shows a shallow minimum close to -0.2 eV. In contrast to the AMF–DMFT model, the MLM and DFT-POL models compare well with PES throughout the entire energy range. Hence, PES does not support the conjecture of a Pu $5f^6$ configuration but rather the more traditional view of $5f^5$.

3. 5f occupation and crystal structure: density-functional theory

The previous sections provide strong experimental support for the $5f^5$ picture of Pu. Here we will show that this 5f occupation number for Pu is entirely consistent with the view of Pu being part of the actinide series of metals. First, we need to point out that DFT has been a remarkably successful tool in not only understanding but also predicting ground-state properties of the actinides. Generally, Th is considered as being the leading actinide because (1) f states are not occupied in Ac and (2) Th is the first metal in the periodic table of elements to have some 5f electrons. Even though this fraction is rather small for Th (~ 0.5), Johansson *et al* [36] showed that it is responsible for the ground-state face-centered cubic (fcc) structure. Eriksson *et al* [37] determined that, due to the promotion of 6d to 5f electrons under compression, Th undergoes a phase transition to a body-centered tetragonal phase isostructural to the ground-state phase of the preceding metal, Pa. DFT calculations are able to very accurately reproduce the measured pressure behavior of the tetragonal distortions observed for Ce and Th, which is linked to the filling of the f band [38]. Söderlind and Eriksson [39] also studied the crystal structure of Pa and predicted a phase transition to a high-pressure face-centered orthorhombic phase very close to that of α-U. This was understood to be a consequence of a subtle pressure-induced increase of the 5f-band occupation in Pa. This new phase was later confirmed by Haire *et al* [40], who used diamond-anvil-cell techniques (DAC). The detailed DAC study of uranium by Akella *et al* [41] showed another case where DFT accurately reproduced the experimental ground-state crystal structure as well as its delicate changes with pressure. In fact, the ground-state structures of all the early actinides (Th–Pu) are correctly determined by careful DFT computations [1]. The agreement between DFT and measured data, as regards the structural behavior of Ce, Th, Pa, and U, indirectly confirms their 5f-band population because of the close relationship [1] between 5f band filling and stable crystal structure.

Clearly, the population and involvement of the 5f states in bonding is of utmost importance for the ground-state properties, including the crystal structures, and DFT provides a unified picture of this relationship for the actinides as described above. In figure 10 we plot the DFT predictions of 6d and 5f occupations for Th–Cm, together with the AMF–DMFT
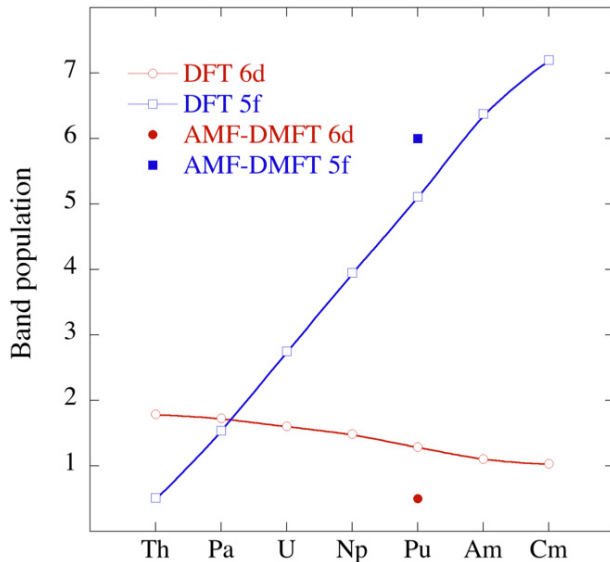
Figure 10. DFT and AMF–DMFT (Pu) 6d and 5f occupation numbers for Th–Cm. The DFT calculations are relativistic and non-magnetic.

Figure 11. Energies for α-U, α-Np, α-Pu, and primitive orthorhombic (p.o.) geometries, relative to the fcc structure, as functions of f-band occupation, within a canonical band-energy model [45].

result for Pu. Notice that the DFT occupation numbers vary smoothly over the series, whereas the Pu AMF–DMFT [8] ($5f^6$) configuration implies a substantial deviation, inconsistent with the overall trend. If this is correct, either Pu is not a member of the actinide series (the occupation numbers should vary smoothly as in the d transition or the rare-earth metals) or the DFT occupation numbers of Th–Np are all incorrect. The arguments put forward in the previous paragraph rule out the latter, while the former is inconsistent with Pu's position in the periodic table.

Note also that DFT predicts Am and Cm to have 6.3 and 7.2 5f electrons, respectively, consistent with a $\sim 5f^6$ configuration for Am discussed in the previous spectroscopy section. Recent high-pressure diamond-anvil-cell experiments for Am and Cm [25] have revealed several phase transitions under compression. These two metals display similar structural behavior under pressure, with the striking exception of an added unique monoclinic ($C2/c$) intermediate phase for Cm. DFT calculations [25, 41–44] have reproduced these phase transitions very accurately, including the formation of the $C2/c$ phase in Cm. This agreement between DFT and DAC gives credence to the predicted occupation numbers because the crystallographic behavior is sensitive to this property [1], as mentioned above. Let us next investigate the link between f occupation and crystal structure in detail, using a simple but transparent model.

The crystal structure dependence on the 5f-band filling was previously investigated [45] by the so-called canonical band theory, when electrostatic interactions and Born–Mayer repulsion were accounted for. Within this model, one can estimate the energy of any geometrical configuration of atoms as a function of the 5f-band population, in analogy to what was done previously to understand the crystal structures of the non-magnetic d-transition [46] and rare-earth [47] metals. Canonical band theory shows that for involvement of three,
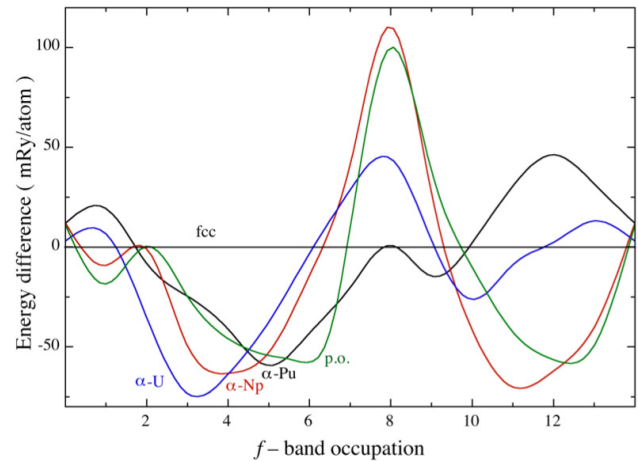
four, and five 5f electrons in the bonding the α-U, α-Np, and α-Pu structures are favored over competing phases. In the present study we again apply this canonical model, with a special interest in the occupation of six 5f electrons, Pu's occupation number according to the AMF–DMFT [10] calculations. In figure 11 we show the structural stability of several phases for f occupations between zero (empty) and 14 (full). Here we are interested in crystal structures that are stabilized by 5f bonding, and leave out the Am ground-state double-hexagonal phase, which is known to be a consequence of 6d bonding. Notice that for six f electrons a primitive orthorhombic phase (p.o.: *Pnma* with $b/a \sim 0.8$, $c/a \sim 0.7$, $x \sim 0.4$, and $z \sim 0.1$) is stable over the α-Pu phase. This suggests that if the $5f^6$ configuration for Pu were correct its ground-state phase would not be the α-Pu structure but rather a primitive orthorhombic (p.o.) or some other unknown structure. Assuming that Am (and not Pu) has six 5f electrons, this corresponds to Am with completely delocalized 5f electrons. At ambient pressure Am is a 'localized' metal with essentially six non-bonding 5f electrons. During compression, however, all 5f orbitals overlap, and at sufficiently high pressure they will 'delocalize', i.e. participate in and even dominate the chemical bonds. Consequently, the canonical band picture predicts a p.o. phase in Am at high pressure and this has indeed been established recently in diamond-anvil-cell work [48] as well as accurate DFT investigations [42–44].

4. Conclusions

Traditionally, Pu has been envisioned to have about five 5f electrons involved in the bonding, which is consistent with band-structure calculations and the general trend of the 5f occupation numbers and crystal structures displayed by the actinides. Recently, a distinct view has been proposed in several publications [8–10, 49] aimed at explaining the lack of credible evidence for significant magnetic moments in Pu. This idea is founded on a localized $5f^6$, americium-like,

configuration in which the $5f_{5/2}$ sub band is fully occupied and hence quenches magnetism in Pu. Consistent with an earlier response [50], we have shown, by three independent measurements (XPS, XAS, and EELS), that this is probably incorrect. More specifically, the δ-Pu calculations with $n = 5.44$ [8], $n = 5.9$ [9], and $n = 5.8$ [10], would each have too much of a $5f^6$ spectral contribution (44%, 90%, and 80%, respectively) to be consistent with the XAS/EELS experimental results. We have further argued that a $5f^6$ configuration in Pu is misleading because it is incompatible with its position in the actinide series and its ground-state monoclinic phase for α-Pu. Thus, all present theoretical approaches have failings and limitations, as is the case for the proposal of a $5f^6$ state in Pu. Additional improvements in modeling are necessary before it can be stated that the physics of Pu is fully understood. However, the objective here was to convincingly argue that it is neither sufficient nor correct to force a non-magnetic '$n = 6$ solution' for Pu upon the longstanding and difficult problem of its 5f electronic structure.

Finally, in a recent article by Shim *et al* [51], an LDA + DMFT calculation with a fluctuating valence and $n = 5.2$ was applied to δ-Pu. The Shim *et al* result is intriguing and stimulating. However, before we can agree that this is the final solution for the δ-Pu electronic structure, a few more questions must be answered. These include experimentally testing the DMFT Kondo-like model for Pu using new measurements such as Fano spectroscopy, as has been done for the Kondo-like system Ce [52], so as to isolate the details of the underlying electron correlation relative to other possible models [53].

Acknowledgments

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