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Coupling between the 4*f* core binding energy and the 5*f* valence band occupation of elemental Pu and Pu-based compounds

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We demonstrate that there is a close coupling between 4*f* core binding energy and 5*f* valence band occupation for Pu-based materials. This enables accurate determination of the valence occupation of this class of materials by simply measuring the 4*f* core binding energy. Our study demonstrates that all allotropes of elemental Pu have a 5*f* occupation close to 5, a finding which is inconsistent with several of the current theoretical models attempting to describe this unique element. A few of the theoretical models proposed for this material are however consistent with our finding; a fact which is discussed in detail.

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Elemental Pu is one of the most complex elements with six allotropes[1] before it melts. Of these, the δ phase stands out as the most mysterious one, and several theoretical and experimental articles have addressed its properties lately.[2–20] The δ phase is stable between 319 °C and 451 °C and crystallizes in an fcc structure. Further, it has a negative thermal-expansion coefficient and a volume which is ~25% greater than that of the low-temperature α phase. In addition, the free energy of the δ and the low-temperature α phase must, at low temperatures, be nearly degenerate, since the addition of a few percent of Al, Ga, In, or Tl stabilizes the δ phase. In an intermediate temperature range the Pu phase diagram shows a β and a γ phase, both which have unique distorted crystal structures and equilibrium volumes which suggest a complex chemical bonding. At temperatures above 451 °C, where the δ phase becomes unstable, there is a face-centered tetragonal phase (δ' phase) and a bcc phase (ϵ) before melting.

Most of the theoretical model attempts to describe the phases of Pu are based on density-functional theory (DFT) electronic structure calculations. It was early recognized that the reasons for these complex properties are indeed connected to peculiarities in the electronic structure, although the details of the complexity in the electronic structure are in themselves heavily debated. Historically, the unique electronic structure of δ-Pu was first recognized by Solovyev *et al.*[2] In this work it was suggested that the Mott transition among the 5*f* shell, which is known to occur as a function of actinide element, does not take place between Pu and Am, as suggested earlier, but within the six allotropes of Pu. In particular it was argued that δ-Pu is on the low-density side of a Mott transition. This idea was elaborated on by Eriksson *et al.*[5] who considered, among the actinide elements, a unique electronic configuration with a partial localization of the 5*f* shell for δ-Pu. A somewhat similar approach was employed using a self-interaction corrected functional.[7] However, subsequent works have mainly focused on two different approaches. The first one to note is the so-called LDA+U method, where a direct term (U), representing the electron-electron repulsion, is added to the effective Hamiltonian of the local-density approximation (LDA). This approach was used in the works in Refs. 8 and 13–15. The second approach is more sophisticated and employs the dynamical mean-field theory (DMFT), in which many-body effects of the band structure are incorporated in an energy dependent but **k**-independent self-energy.[21] Several works based on DMFT have been successful in reproducing the equilibrium volume or lattice dynamics of Pu.[10,11] Finally it should be noted that normal electronic structure calculations using an effective Hamiltonian as given by the local spin-density approximation (LSDA) also reproduce much of the crystal chemistry of δ-Pu, e.g., the equilibrium volume, provided that the calculations are done in a spin-polarized mode, where an antiferromagnetic configuration is found to have lowest energy.[3,4] It is very important to note however that no long-range magnetism has been detected in δ-Pu. The absence of ferromagnetism in δ-Pu was actually analyzed early on by a relativistic formulation of Stoner theory.[22]

The different theoretical models listed above differ in significant and fundamental ways from each other. Nevertheless, they are more or less equally successful in reproducing ground-state properties of δ-Pu (equilibrium volume, elasticity) and in some cases even photoelectron spectra.[3,6,12] This is naturally an unsatisfactory situation, and one needs to find additional experimental information with which to make further comparisons to shed light on which model is appropriate. As we will demonstrate in this paper the occupation of the 5*f* shell is a decisive diagnostic property available from theory and experiment, primarily since it couples closely to the 4*f* core-level binding energy, hence enabling deduction of the 5*f* occupation by an analysis of experimental data alone.

An inspection of the different theoretical calculations reveals that the property which differs the most for the various models proposed for Pu is the occupation of the 5*f* valence states. Some of the theoretical works conclude that the occupation of the 5*f* shell in δ-Pu is very close to 5.[2–5,8] Deviations from this pattern are found in the LDA+U calculations[13,14] and the DMFT calculation of Ref. 15 which tends to push the *f* occupation up to between 5.4 and 6. An

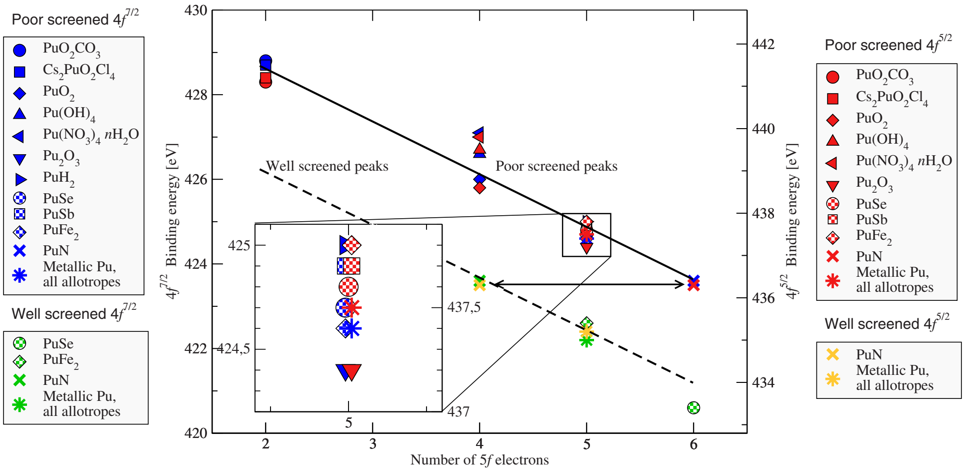

FIG. 1. (Color online) Binding energies (Refs. 17 and 32–44) vs $5f$ occupation numbers for the materials of this study. Blue (dark gray) symbols are for poor-screened $4f^{7/2}$ peaks; red (medium dark gray) are for poor-screened $4f^{5/2}$ peaks. The green (medium light gray) and yellow (light gray) symbols are for well-screened $4f^{7/2}$ and $4f^{5/2}$, respectively. The $4f^{7/2}$ scale is to the left and the $4f^{5/2}$ scale is to the right. Both scales span 10 eV and have been offset so that the symbols of the $4f^{5/2}$ and $4f^{7/2}$ binding energy of Pu_2O_3 lie on top of each other in the figure.

experimental measurement of the $5f$ occupation of δ-Pu would be extremely useful, since a direct comparison to theory could then exclude one or several of the theoretical models. Here a comparison to the $5f$ occupation of the other phases of Pu, especially the α phase, is interesting since it is well established that the $5f$ occupation in this phase is close to 5.[23,24] Unfortunately, observation of a partial occupancy is difficult and often relies on the interpretation of, for plutonium compounds, the notoriously complex valence spectrum. Hence, additional types of analysis would be beneficial, and we will demonstrate that the $4f$ core-level binding energy is coupled to the occupation of the $5f$ shell. Our analysis is based only on experimental results and is not influenced by approximations necessary in a theoretical model.

We obtain $4f$ core binding energies of plutonium in a number of compounds from previously published data from electron spectroscopy for chemical analysis (ESCA) (Refs. 25 and 26)—a well established method for determining binding energies in solids. In this experiment the $4f$ binding energy can be characterized by a so-called well-screened and a poor-screened peak,[27] which reflects the different screening channels of the $4f$ core hole. We wish to investigate the possible connection between the $4f$ binding energy and the number of $5f$ electrons in Pu and Pu-based materials. We do this by analyzing binding energies for a number of plutonium compounds for which we can ascertain an accurate $5f$ electron count by some means and we investigate the coupling between $5f$ electron occupation and $4f$ core-level binding energy. Only a small number of compounds, among them the different phases of pure plutonium, show both well-screened and poor-screened peaks, as the $5f$ electrons in most compounds studied here have localized $5f$ states and only the poor-screening channel appears.

To establish a connection between core-level binding energy and the number of $5f$ electrons we need to obtain a reliable $5f$ electron count at least for a few reference materials. We do this in two ways, depending on the nature of the material. For compounds which are insulators, we simply use the formal oxidation number, for example, PuO_2 has an oxidation number of 4+ for Pu, which is well known to result in an $5f^4$ electronic configuration, i.e., the number of $5f$ electrons is 4. For metallic compounds, this way of assigning a $5f$ count cannot be applied. Instead we use determinations obtained by neutron experiments, magnetometry, and resistivity data.[28–31] We will discuss below, how we evaluated the $5f$ occupation for each metallic system.

Our analysis is based on experimental values for some 15 allotropes of Pu or Pu-based compounds. The measured binding energies are shown in Fig. 1. It can be seen that a linear relationship can be tied between the $4f$ binding energy and the $5f$ occupation. This is clearest when inspecting the poor-screened $4f$ peak. Figure 1 shows that the lower the occupation of the $5f$ shell, the larger the binding energy. It may also be seen that within a f^n configuration there is a spread in the binding energies. This is mostly clear for the f^4 configuration, where the spread is over 1 eV. This naturally reflects the fact that among the compounds which are identified with an f^4 configuration, the ionicity of the ligand atoms or ligand complexes will be different, which results in a variation in the amount of valence *spd* electrons around the Pu atom and hence a chemical shift.[50] In Fig. 1 we have identified compounds with a $5f$ occupation of 2 (e.g., for PuO_2CaO_3), 4 (e.g., PuO_2), and 5 (e.g., Pu_2O_3). The identification of these occupations is straightforward and follows well-established rules of oxidation numbers. Among the metallic compounds investigated here a $5f$ occupation of 5 has been discussed for most of the Laves phase compounds[28] (e.g., $PuFe_2$). It is also obvious that all allotropes of elemental Pu and Pu-Am alloys fall on the straight line in Fig. 1 if a $5f$ occupation close to 5 is attributed to them. The relation thus obtained between $4f$ binding energy and $5f$ occupation is that a change in $5f$ occupation of 1 electron brings about a shift of the $4f$ binding energy of about 1.2 eV.

A few of the compounds shown in Fig. 1 need special analysis. For instance, the binding energy of PuN falls on the line describing the linear relationship between 5f occupation and binding energy if one assumes a f^6 configuration for this compound. An f^6 configuration in plutonium compounds is often said to result in what is known as a "closed-shell" configuration by filling of the $f^{5/2}$ single-electron spin-orbit level, and therefore resulting in certain physical properties, such as a low specific-heat capacity. While this would indeed be true in a single-electron band picture, there are examples such as Pr where many-body effects cause a large increase of the effective mass of the localized f electrons.[45] The magnetic properties of PuN are also unexpected,[30] and a designation of an f^6 configuration may possibly also explain this behavior. Also, PuSe has a poor-screened peak suggesting a f^5 configuration and a well-screened peak which is closer to what one would expect for a f^6 configuration. The latter behavior is of course not unexpected if a mixed-valency configuration is stable, where in the final-state process one of the two components to this configurations is more pronounced than the other. This lends additional support to the analyses of Wachter[46] and Oppeneer *et al.*[47] for Pu chalcogenides, which suggest a mixed-valence configuration with a 5f occupation between 5 and 6. As the formal oxidation state of these compounds is (II), this seems a reasonable designation. We also note that the similar slope of the curves for the well-screened and the poor-screened peaks, together with the fact that the displacement of spectral weight between the screening channels in the plutonium compound or intermetallic compounds does not seem to move the position of the peaks, makes us confident that the correlation between the 4f binding energy and 5f occupation is insensitive to the degree of localization of the 5f states.

Figure 1 demonstrates that the slightest change in 5f occupation and/or ionicity of ligand states immediately shows up in a substantial core-level shift. The fact that all phases of elemental Pu have the same binding energy forms a very compelling argument that they have very similar 5f occupations. Among the Pu allotropes the 5f occupation has been easiest to identify for the α phase, since the effect of strong correlation is not dramatic here and regular electronic structure theory works well in reproducing ground-state properties.[23] From these studies one has drawn the conclusion that the 5f valence state of α-Pu contains close to 5 electrons.

When discussing the 5f occupation of a theoretical calculation it is important to note that this number necessarily depends on the volume in space for which the charge density is integrated. Hence the 5f occupation depends on if an atomic sphere approximation (ASA) is used or if a muffin-tin based full potential method has been used. In the latter case the occupation numbers also depend on the size of the muffin-tin radius used for defining the base geometry in the calculations. Independent on which approach one uses, most theories conclude that the 5f occupation on all phases of Pu deviate with less than 0.1. This is for instance the result of the ASA calculation of van Ek *et al.*[48] and the full potential calculation of Söderlind *et al.*[23] If a full-potential geometry with touching muffin-tin radii of δ-Pu is used, calculations using the local-density approximation or the generalized gradient approximation result in a 5f occupation close to 5. This occupation number fits nicely into the general trend exhibited in Fig. 1 and we draw the conclusion that all phases of elemental Pu must have an occupation of the 5f shell which deviates marginally from 5. This also compares well with early analyses of elemental plutonium,[49] an Anderson model analysis of the ESCA spectrum,[17] atomic simulations,[18] and some more recent LDA+DMFT results.[12,16]

A valence band f count of all phases of elemental Pu close to 5 is the primary result of our study. This is consistent with the analysis by Johansson and Rosengren[49] of Pu, where it was shown that the f^5 configuration is stable compared to the f^4 and f^6 configurations, approximately with 2.5 and 1.5 eV, respectively. The present analysis, as well as that in Ref. 49, relies only on experimental data, which makes the obtained result reliable for deciding on the quality of different theoretical models for Pu metal. Our analysis hence establishes a means with which to assess the quality of a theoretical model for Pu-based materials, and it seems that the calculations of Refs. 13–15 are not consistent with the criterion of a similarity in occupation of the 5f valence states of all allotropes of metallic Pu and that this occupation is close to 5. Unfortunately the calculated 5f occupation was not quoted in Refs. 8, 10, and 11, so it is difficult to analyze these theories in connection to the data in Fig. 1. In Ref. 12 a mixed-valency behavior was quoted with an average 5f occupation of 5.2, a number which seems slightly large, but cannot be refuted by the analysis presented here. However, unlike the Pu chalcogenides, there is no direct experimental evidence for a mixed-valent state in δ-Pu. The works of Refs. 3–5 and 24 give 5f occupation numbers close to 5 and are hence consistent with the analysis of the experimental data of Fig. 1.

The reason for the large scatter in 5f valence band occupation of the different theoretical models most likely has its origin in the different approximations to the so-called double-counting term. This term corresponds to interactions already present in the part of the effective potential which has its origin from the uniform electron-gas approximation (or the gradient expanded potential). Once an additional interaction is added to this potential, one must subtract off the part which was already included in the contribution from the DFT approximation to the exchange-correlation potential, derived from the uniform electron gas, so that interactions are not included more than once, hence the name double counting. Our analysis suggests that the double-counting approximation used in Refs. 13–15, the so-called around mean-field limit, is not appropriate for Pu (or Pu-based systems) since it results in 5f occupations which deviate in an unacceptable way from the expected number of 5. It is likely that this conclusion holds in general for actinide materials.

In addition to providing information on the 5f occupancy of the different phases of Pu, the identified correlation between 4f core binding energy and 5f occupation might be useful in establishing the valence band configuration for Pu-based compounds and alloys in general.

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[50] See, e.g., Ref. 35, where the variations of binding energies in the $4f$ shell of various oxides are precisely matched by shifts in the oxygen $1s$ shell and so can be ascribed to changes in the chemical bond between oxygen and plutonium. If that small shift is accounted for the binding energy of $Pu(OH)_4$ ends up on top of PuO_2.