SIC-LSD study of δ-Pu and $PuO_{2\pm x}$

L. Petit[1,2], A. Svane[2], Z. Szotek[3], and W.M. Temmerman[3]

[1] *Computer Science and Mathematics Division, and Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

[2] *Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*

[3] *Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK*

Abstract

The electronic structures of actinide solid systems are calculated using the self-interaction corrected local spin density approximation. Within this scheme the $5f$ electron manifold is considered to consist of both localized and delocalized states, and by varying their relative proportions the energetically most favourable (ground state) configuration can be established. Specifically, we discuss elemental Pu in its δ-phase, and the effects of adding O to PuO_2.

The quantum-mechanical understanding of the physics of actinides and their compounds presents a challenge due to the intricate nature of the partially filled $5f$-shell. Compared to the rare earth $4f$-states, the $5f$ states in the actinides are less inert and can play a significant role in bonding, depending on the specific actinide element and the chemical environment. This is most convincingly demonstrated in the elemental metals, for which a localization transition occurs when going from Pu to Am.[1]

Pu lies on the borderline between itinerant and localized f-electron behaviour. Its very complex phase diagram implies that the f-electron properties are of particularly intricate nature. The ground state of the α-phase is well reproduced by LDA calculations[2], but the high temperature δ-phase is peculiar. Its crystal structure is the high-symmetry fcc, and it has the largest specific volume of all Pu allotropes (25 % larger than that of α-Pu), and the thermal expansion coefficient is negative. It has long been recognized that these facts are connected to a higher degree of localization of the f-electrons in the δ-phase, although its volume is still $\sim 16\%$ smaller than that of Am.

Recently, the self-interaction corrected (SIC)-LSD method [3, 4] was applied to the series of actinide metals[5] from Np to Fm, correctly describing the itinerant nature of Np, the trivalency of Am, Cm, Bk and Cf, and the shift to divalency in Es and Fm. In the SIC-LSD formulation one deals with two types of f electrons,

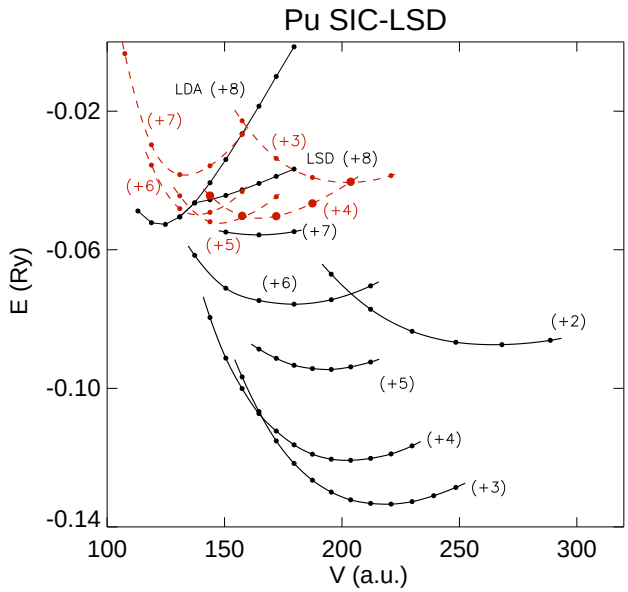

Figure 1: Total energy for δ-Pu. Dashed curves assume $j-j$ coupled localized f^n shell, solid curves assume $L-S$ coupling.

the localized and hybridized f electrons. By assuming different f^n configurations of localized electrons, various valency configurations can be realized and studied in detail. For a given f^n configuration, the minimum in the total energy as a function of lattice parameter determines the equilibrium lattice constant. By comparing the total energy minima for different f^n configurations, the global ground state configuration and lattice constant can be determined.

The SIC-LSD results for the δ-phase of Pu are summarized in Fig. 1, where the calculated total energies for different localized f^n configurations are plotted as functions of volume. To describe different localized configurations, we have considered both $L-S$ (solid curves) and $j-j$ couplings (dashed curves) of the f-states. The lowest energy has been found for a localized $L-S$ coupled f^5 shell, corresponding to trivalent Pu atoms.[5] The corresponding equilibrium volume is 218 a_0^3, which is 30 % larger than the experimental volume of δ-Pu. Clearly, this is not an adequate description of δ-Pu. Localizing one more f-electron leads to an even larger volume and also a larger total energy, while fewer localized electrons lead to smaller equilibrium volumes, but also larger total energies. The best agreement with the experimental volume within the $L-S$ coupling scheme is obtained for the f^2 localized scenario. The $j-j$ coupling scheme, on the other hand, leads to a completely different picture. In this case the

scenarios with localized f^2, f^3, and f^4 shells are almost degenerate in energy, with f^3 having the lowest energy, and the corresponding equilibrium volume 12% *smaller* than the experimental volume of δ-Pu. By taking $j-j$ coupled localized shells, one artificially turns the spin-density contribution to the total energy off, and this is why an improved description is obtained. This does **not** mean, however, that the $j-j$ coupled Pu f^3 shell is the correct ground state of Pu, but that within the restricted one-electron picture the $j-j$ coupled f localized shell is a better representation of the true ground state. Our SIC-LSD study seems to demonstrate that more complicated ground states are called for, as the true ground state should provide an adequate description of spin fluctuations, leading to quenching of the Pu moment, as well as fluctuations in the number of localized f-electrons should be accounted for.

As already mentioned, δ-Pu is a special case in the actinide series. When going to Am, the $L-S$ ground state obtained with the SIC-LSD approach is quite adequate, leading to a localized f^6, $M_S = 3$, $M_L = 3$, i.e., $J = 0$ ground state. The equilibrium volume is $\sim$ 8% larger than the experimental volume, which is acceptable. The importance of magnetic exchange interactions remains contested in the case of δ-Pu,[6] but by artificially setting the exchange interaction to zero, a much improved lattice constant has been obtained, as also found by Refs. [7] and [8]. Since experiments find Pu to be non-magnetic, one must conclude that the mean-field approaches of LSD and SIC-LSD overestimate the tendency towards magnetic moment formation, by not taking into account quantum fluctuations in the f-shell. The latter was corroborated by the calculations of Savrasov *et al.*[9], who obtained a satisfactory description of δ-Pu by taking into account dynamical fluctuations.

In contrast to δ-Pu, the SIC-LSD method finds the correct ground state for the stoichiometric PuO_2 compound. In agreement with experiment, Pu in this compound is found to be tetravalent, with a localized f^4 shell. The oxygen p bands are filled, and a large insulating gap is obtained. PuO_2 has been the favored compound for storage of Pu from nuclear waste. However, recently the chemical inertness of PuO_2 has been questioned, in particular regarding its possible reaction with water, leading to further oxidation and formation of PuO_{2+x}.[10]

With the SIC-LSD method we have investigated[11] the PuO_{2+x} system, by constructing a supercell with four PuO_2 units and an additional O atom in the interstitial region, constituting a model of a $PuO_{2.25}$ compound. As can be seen in Fig. 2, the inclusion of the extra O atom into the fluorite lattice has a profound effect on the

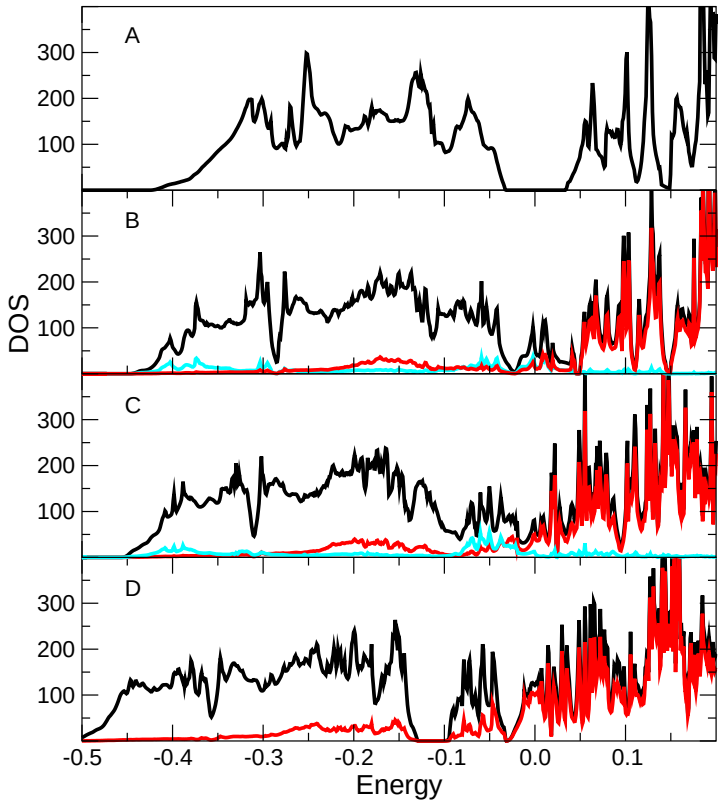

Figure 2: Total DOS (black), Pu f-projected DOS (red) and interstitial O p-projected DOS (blue).

calculated electronic structure. In the two top panels of the figure, we compare the densities of states (DOS) for the valence and conduction bands of $Pu_4^{4+}O_8$ (Fig. 2a) and $Pu_4^{4+}O_9$ (Fig. 2b). Both scenarios refer to the cases with localized f^4 configurations on all the Pu sites. In the case of Pu_4O_9, a broad band, originating from the p-p overlap between neighbouring interstitial O atoms, spans the energy range where in Pu_4O_8 an insulating gap, of 0.94 eV, is observed. The position of the Fermi level indicates that this p-band is only partially filled, which is due to the fact that only four valence p states of the added O atom are occupied.

To investigate whether one can populate further the O impurity band states, by delocalizing f-electrons on the neighbouring Pu atoms, we have gradually replaced Pu sites with the f^4 configuration by Pu sites with the f^3 configuration. Figure 2c corresponds to the situation where two additional f-electrons have been delocalized ($Pu_2^{5+}Pu_2^{4+}O_9$ configuration). Note that the two extra itinerant electrons (compared to the situation in Fig. 2b) are accommodated in the impurity O p band, as a result

of charge transfer and Pu-O hybridization, indicated by the upwards shift of the Fermi level. This is associated with a large gain in charge transfer and hybridization energy. The delocalized f-states give rise to an additional narrow f-peak, which occurs above the Fermi level, thus remaining unoccupied. In Fig. 2d, also a third and fourth electron have been delocalized, resulting in an f^3 configuration on all Pu sites ($Pu_4^{5+}O_9$). It can be seen that, with the p-band being filled by the first two delocalized electrons, these further two electrons have to start filling the narrow f-peak. The corresponding gain in band formation energy is small, essentially balancing out the loss in SIC energy. The energy gains for delocalizing one f-electron per Pu site, are 54 mRy, 21 mRy, 6.4 mRy, and 4.8 mRy, for respectively the first, second, third, and fourth f-electron. It thus follows from our investigation that the energetically favourable ground state configuration is $Pu_4^{5+}O_9$, i.e. that the insertion of O into PuO_2 increases the Pu oxidation from four to five. No higher oxidation state can be realized, as delocalizing a second f-electron from the same Pu site ($Pu^{6+}Pu_3^{4+}O_9$) turns out to be energetically unfavourable.

Our SIC-LSD study shows that the nearest neighbour Pu atoms, to the interstitial O, transform to the pentavalent configuration by delocalizing one f-electron, which is donated to the extra O to form hybridized states, occuring in the gap-region of the pure PuO_2 compound. Similarly, an O vacancy in PuO_2 will lead to the formation of trivalent f^5 Pu ions in the vicinity of the vacancy. In effect, the localized f^n shell of Pu acts as a reservoir for absorbing or releasing electrons to be accomodated by the chemical bonds of the O atoms. Whether the oxidation process actually takes place depends on the thermodynamic conditions, in particular the chemical potential of the additional oxygen. At T=0K, the Pu dioxide appears to be stable, but it is not inconceivable that under different conditions the oxidation may occur.

In summary, we have discussed the electronic properties of Pu and PuO_{2+x}, as obtained within SIC-LSD approach. We have shown that this approach is well suited to describe trends regarding lattice parameters and valencies of these systems. It works especially well for systems with well localized f-shells. It also indicates that the ground state of δ-Plutonium is more complex than the SIC-LSD can describe and thus underlines the need of developing a dynamic generalization of the SIC-LSD approach.

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