Coulomb-$U$ and magnetic moment collapse in $\delta$-Pu

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Abstract. – The around-the-mean-field version of the LDA+U method is applied to investigate electron correlation effects in $\delta$-Pu. It yields a non-magnetic ground state of $\delta$-Pu, and provides a good agreement with experimental equilibrium volume, bulk modulus and explains important features of the photoelectron spectra.

Plutonium is probably the most intricate element from the point of view of condensed matter physics. It exhibits six allotropic modifications at ambient pressure, some of them of very low symmetry (monoclinic), and there is little doubt that the anomalous behaviour is related to the 5$f$ electronic states, being at the borderline between the localized, non-bonding, behaviour and the bonding situation of electronic bands. One can preconceive that at the cross-over regime, several states with very different degree of 5$f$ delocalization can be nearly degenerated in energy.

The most thoroughly studied phases are $\alpha$-Pu (monoclinic) and $\delta$-Pu ($f$cc). The latter is stable between 592 and 724 K, but can be stabilized down to $T = 0$ K by various dopants. This phase has the largest volume (by 20\% higher than $\alpha$-Pu) (for overview see Ref. [1] and references therein).

The atomic volume is an important indicator of the situation of the 5$f$-electronic states. Withdrawing of the 5$f$ states from the bonding and confining them in the ionic core leads to a significant volume expansion. On the plot of atomic volumes of elements, Pu ($\alpha$) represents a continuation of light actinides, with the decreasing branch resembling the parabolic behavior of transition metals. On the other hand, heavy actinides, starting with Am ($Z = 95$), display higher volume, following a weakly decreasing volume of lanthanides, characterized by non-bonding 4$f$ states. $\delta$-Pu, being half way between the volume of $\alpha$-Pu and Am, represents therefore generally the cross-over regime, where electron-electron correlations play a prominent role.

Ab-initio electron energy calculations based on the Density Functional Theory (DFT) in the Local Density (LDA) or Generalized Gradient (GGA) approximations account generally well for basic properties of metallic systems. Numerous variants of this successful paradigm were applied to Pu phases. The most conspicuous failure is the case of $\delta$-Pu calculations which...
inevitably lead to magnetic ordering. The fact that the lattice expansion due to magnetism yields approximately correct value of the volume, and intrasingle of magnetic order within the DFT theory both within the LDA and GGA approximations, led to speculations about magnetic ordering of $\delta$-Pu. But it contradicts experimental findings (magnetic susceptibility has a character of weak Pauli paramagnet [2], paramagnetic state is also evidenced by $^{27}$Al NMR [3], $^{69}$Ga NMR [4] and neutron scattering [5]). Since its first occurrence [6], new claims of magnetic Pu keep filling research journals; there is already a debate about the detailed type of order, and recently even other Pu phases were assumed as magnetic [7]. One common feature of light actinides is that orbital moments, appearing due to the strong spin-orbit interaction in the case of spin polarization, are oriented antiparallel to spin moments. LDA or GGA calculations of $\delta$-Pu (with approximately five $5f$ electrons) lead to the spin moment larger than orbital moment (which is opposite to what the Hund’s rules assume for the $5f^5$ ionic state), but the existence of "exact" accidental complete cancellation can be doubted. The systematic cancellation appears only for the $5f^6$ configuration of Am (both for the $LS$ and $jj$ coupling).

Pu magnetism as an undesirable artefact tends to appear also in other approaches, like the mixed-scheme model, based on minimization of energy for the localized $5f^4$ configuration, while the remaining $5f$ electrons form a band [8], while the Dynamical Mean Field Theory (DMFT) deduces that magnetic order is washed out by dynamical fluctuations of moments [9]. As yet, the challenging question and the real problem of Pu remains, which is why is there no magnetism in the $\delta$-Pu phase?

Here, we address this problem making use of a well known L(S)DA+U method. Generally, the LDA+U calculations account for the on-site correlations between the $f$ electrons in a more realistic way than the LSDA. First applied to $\delta$-Pu by Bouchet et al. [10], they also lead to a magnetic solution, similar to that reported by Savrasov and Kotliar [11]. In a contrary to [10, 11], we apply to $\delta$-Pu a different version of the LDA+U method which is based on the original LDA+U total energy functional of Ref. [12]. We show that when the LDA+U of Ref. [12] is reformulated in a spin and orbital rotationally invariant form, it yields a basically non-magnetic $\delta$-Pu with $S \rightarrow 0$ and $L \rightarrow 0$.

The correlated band theory L(S)DA+U method consists of the local spin-density approximation (LSDA) augmented by a correcting energy of a multiband Hubbard type $E_{ee}$ and a “double-counting” subtraction term $E_{dc}$, which accounts approximately for an electron-electron interaction energy already included in LSDA. It is well known that the form of “Coulomb-U” correction to the LDA is not uniquely defined [13]. The most commonly used is the version of LDA+U total energy functional in a so-called “fully localized” limit (FLL) [11, 14], in which the double-counting term $E_{dc}$ is taken to satisfy an atomic-like limit of the LDA total energy.

Another and historically the first LDA+U functional is often called as an “around-mean-field” (AMF) limit of the LDA+U. In this AMF-LDA+U limit [12, 15] the interaction energy takes the form

$$E_{ee}^{AMF} = \frac{1}{2} \sum_{\gamma_1, \gamma_2, \gamma_3, \gamma_4} \delta n_{\gamma_1, \gamma_2} \left[ \langle \gamma_1, \gamma_3 | V_{ee} | \gamma_2, \gamma_4 \rangle - \langle \gamma_1, \gamma_3 | V_{ee} | \gamma_4, \gamma_2 \rangle \right] \delta n_{\gamma_3, \gamma_4},$$

where $V_{ee}$ is an effective on-site “Coulomb-U” interaction, the combined spin-orbital index $\gamma = (m\sigma)$ is composed from the angular $m$ and spin index $\sigma$, and

$$\delta n_{\gamma_1, \gamma_2} = n_{\gamma_1, \gamma_2} - n^{\sigma_1} \delta_{\gamma_1, \gamma_2}, \quad n^{\sigma} = \frac{1}{2l + 1} \sum_{m=-l}^{l} n_{m\sigma, m\sigma}.$$
where \( n_{\gamma_1 \gamma_2} \) is the on-site \( f \)-occupation matrix in the spin-orbital space which has to be defined with respect to the chosen localized orbital basis set, and \( n^\sigma \) is an average spin-orbital occupation. The double-counting correction is set equal to zero, \( E_{dc}^{AMF} = 0 \).

We note that the essential feature of the Eq. (1) is the presence of spin-off-diagonal elements of the on-site occupation matrix \( n_{\gamma_1 \gamma_2} \equiv n_{m_1 \sigma_1, m_2 \sigma_2} \) which are in general non-zero in the presence of the spin-orbit coupling (SOC).

As it was shown recently in Ref. [13], the AMF-LDA+U formulation is most appropriate for metallic phases in which the Coulomb-\( U \) is comparable to the bandwith \( W \). On the other hand, the FLL-LDA+U model is more suitable for insulators, with Coulomb-\( U \) much larger than \( W \). Here we have extended the AMF-LDA+U for the general spin and orbital rotationally invariant case including the SOC, and implemented it in the full potential linearized augmented plane wave (FP-LAPW) basis in a way similar to a previous relativistic FLL-LDA+U FP-LAPW implementation [16].

We calculated the electronic and magnetic structure of \( \delta \)-Pu using three different approaches: (i) LSDA, (ii) FLL-LDA+U, and (iii) AMF-LDA+U. In all these calculations, we assumed a tetragonal unit cell with two Pu atoms in order to accommodate the anti-ferromagnetic (AFM) order, as it is well known that both the LSDA [17] and GGA [18] yield the AFM as the ground state of Pu.

| Model          | \( M_S \) | \( M_L \) | \( M_J \) | \( V_{eq} \) | \( B \) (kbar) |
|----------------|----------|----------|----------|------------|-------------|
| LSDA           | 4.357    | −2.020   | 2.337    | 136.8      | 761         |
| FLL LSDA+U     | 3.272    | −3.802   | −0.530   | 187.9      | 675         |
| AMF LSDA+U     | ∼0       | ∼0       | ∼0       | 181.5      | 314         |
| Experiment     | N/A      | N/A      | 0        | 168        | 299         |

The spin \( M_S \), orbital \( M_L \) and total \( M_J \) magnetic moments on Pu atom calculated within the LSDA (see Table I) are in a very good agreement with previous LSDA calculations [17]. Starting from the LSDA calculated charge and spin densities and on-site spin and orbital occupations, we performed the LDA+U calculations. We choose \( U = 4 \) eV and exchange interaction \( J = 0.7 \) eV in the range of commonly accepted values for Pu [11]. The FLL-LDA+U model yields a substantial (approx. 1 \( \mu_B \)) reduction of \( M_S \) and an increase of \( |M_L| \) by approximately 2 \( \mu_B \), resulting in a substantial reduction of the \( |M_J| \) (see Table I), while keeping non-zero local magnetic moment on Pu atom [19]. The Coulomb-\( U \) has a strong effect on both the spin and orbital polarization, but it changes very little the total \( f \)-state occupation \( n_f \) – from approximately 5.06 in LSDA to 4.95 in FLL-LDA+U. With the increase of \( U \) from 4 eV to 5 eV, the \( M_S \) increased to 3.42 \( \mu_B \) and \( M_L \) decreased to −3.97 \( \mu_B \), yielding a slight increase of \( |M_J| \) to 0.55 \( \mu_B \) and a decrease of \( n_f \) to 4.93. Thus, in spite of major differences in the values of the \( M_S \), \( M_L \), and \( M_J \), both the LSDA and FLL-LDA+U calculations describe \( \delta \)-Pu as a \( 5f^5 \) state.

Next, we turn to the salient aspect of our investigation, the AMF-LDA+U (\( U = 4 \) eV, \( J = 0.7 \) eV) calculations. Starting from strongly spin-polarized LSDA charge and spin densities and \( 5f \) manifold spin and orbital occupations and without any constraint, the calculations converged to the almost zero magnetic moment with remaining \( M_S \) and \( |M_L| \) less than 0.01
Fig. 1 – Spin $M_S$, orbital $M_L$, and total $M_J$ magnetic moments dependence on the Coulomb-$U$ as calculated in AMF-LDA+U model for the experimental lattice parameter $a = 8.760$ a.u.

Fig. 2 – Total energy as a function of the volume per Pu atom calculated within the AMF-LSDA+U ($U = 4$, $J = 0.7$ eV) and LSDA in the antiferromagnetic model.

$\mu_B$. We also performed the calculations starting from a different FLL-LDA+U ground state and obtained essentially the same results. We conclude that the AMF-LDA+U yields fundamentally non-magnetic $\delta$-Pu, in accordance with experimental observations. Importantly, the $5f$ occupation $n_f$ is increased substantially from $n_f \approx 5$ in LSDA and FLL-LDA+U to $n_f = 5.44$ (see Table I) meaning that there is a substantial deviation from the $5f^5$ ionic state.

The dependence of the spin $M_S$, orbital $M_L$, and total $M_J$ calculated within the AMF-LDA+U on the value of Coulomb-$U$ is shown in Fig. 1. For small values of $U$ ($\approx J$), $\delta$-Pu is magnetic with sizeable $M_S$ and $M_L$ moments that almost cancel each other. As the $U$ value is increased to 1.5 eV, the local moments $M_S$ and $M_L$ disappear and $\delta$-Pu is non-magnetic for realistic values of the Coulomb-$U$ (from 3 to 5 eV). It is interesting to note that $n_f$ also depends on $U$ and it increases from $n_f = 5.1$ ($U = 0.5$ eV) to $n_f = 5.5$ ($U = 5$ eV).

The total energy dependence on the volume per Pu atom calculated within the AMF-LDA+U ($U = 4$ eV) is shown in Fig. 2 and compared with the results of the AFM LSDA calculations. First, we mention that the AFM LSDA yields the equilibrium volume $V_{eq}$ 136.8 (a.u.)$^3$ per Pu and bulk modulus $B = 761$ kbar (see Table I), in a good agreement with the LMTO results of Ref. [17]. The LSDA $V_{eq}$ is close to $\alpha$-Pu value 134 (a.u.)$^3$ which is approximately by 20 % smaller than the experimental volume 168 (a.u.)$^3$ of $\delta$-Pu, while the bulk modulus is almost twice bigger than its experimental value 299 kbar [20]. As it was already shown in [10,11], the FLL-LDA+U model gives the $V_{eq}$ close to the experimental $\delta$-Pu volume and it slightly lowers the bulk modulus (see Table I). Finally, the AMF-LDA+U yields $V_{eq} = 181.5$ eV and $B = 314$ kbar (see Table I and Fig. 1) which are in a very good agreement with experimental data. As yet, the Coulomb-$U$ is treated as an adjustable parameter and $V_{eq}$ can be fitted further to the experiment by a slight decrease of $U$. However, it is clear that the conventional value $U = 4$ eV works already quite well. Thus, the AMF-LDA+U is shown to give the best agreement with experiment both for magnetic and structural properties of the $\delta$-Pu.

In Fig. 3(a) we show the total (TDOS, per unit cell) and $f$-states projected densities of states (fDOS) resulting from the $\delta$-Pu bulk AMF-LDA+U calculations. In order to clarify the character of the $5f$ manifold resulting from the AMF-LDA+U calculations, it is convenient
to look at the $j_z = m_l + m_s$ fDOS shown in Fig. 3(b), as the z-projection of the total moment $j_z$ is the only remaining quantum number in the presence of the SOC and magnetic polarization. It shows six filled $j = 5/2$ f-states and the $j = 7/2$ f-states that are split away by approximately $4-5$ eV. As the LDA+U model is not based on any kind of atomic coupling scheme (LS or $jj$) it rather determines the set of single-particle orbitals that minimize variationally the total energy. The LDA+U result can be interpreted as yielding the ground-state configuration that corresponds to the $jj$-coupled Slater determinant formed of six $j = 5/2$ orbitals. Further, taking into account the finite ($\approx 2$ eV) width of the f-band and the occupation $n_f = 5.44$, we can interpret the calculated ground state as a partially localized $f^6$ manifold hybridized with a broad valence band (see Fig. 3(a)).

An important criterion for assessment of results of electronic structure calculations is given by electron spectroscopies. Although some techniques, as BIS, have not been applied on Pu yet, there exists high-resolution Ultraviolet Photoelectron Spectroscopy (UPS) data, mapping
the electronic structure down to about 10 eV below $E_F$ [21,23–25], while X-ray photoelectron spectroscopy [21, 24, 25] gives information on the screening of a deep core-hole by conduction electrons.

Valence-band spectra of $\delta$–Pu and handful of other Pu-based systems studied so far exhibit invariably three narrow features, one at $E_F$ or in its close vicinity, the other two at 0.5 and 0.85 eV below $E_F$, which are called A, B, and C, respectively. Some systems exhibit also another, broader, separate feature D, the energy of which varies between compounds, and which is not noticeable for $\delta$–Pu. It was argued [24] that the intensity of D reflects the degree of 5$f$ localization. For example, the peaks A-C are absent in the 5$f$ localized compound PuSb [26], and all the 5$f$ spectral intensity is concentrated in the broad peak D.

Valence-band photoelectron spectra reflect to some extent the density of occupied states in the ground state (DOS). A comparison with the bulk experimental UPS [21, 24] (see Fig. 3(c)) shows that LDA+U places the 5$f$ manifold approximately 0.9 eV below the Fermi energy ($E_F$) in accordance with the experimental C peak position, while it does not resolve correctly the experimental features A and B at the $E_F$ edge.

As discussed in Ref. [22], the sharp features A-C are not specific for individual compounds, but they appear at invariable energies over a class of diverse Pu systems. It is therefore implausible that they could be related to any ground-state one electron states. Dismissing the peaks A-C from the comparison, as we assume them either to be due to the final-state effects, which could be reconciled with the 5$f^5$ final-state multiplet [27], or due to a general many body phenomenon (analogy of a Kondo effect) [28]), we are left at a difficult situation, as no other well-defined feature is seen in the UPS spectra. But for ultrathin layers, with thickness varying down to about one monolayer (see Fig. 3(c)), a broad, but well defined peak D, centered at 1.6 eV binding energy, concentrates most of the 5$f$ spectral intensity, whereas the peaks A-C (still at their energies) become barely noticeable.

Therefore we undertook analogous AMF-LDA+U calculations for free-standing Pu slabs (where the number of Pu-layers varies from 1 to 5) with the lattice parameter identical to that of $\delta$–Pu. For the one monolayer (1ML) (see Fig. 3(d)), the 5$f$ states form a very narrow band at 1.5 eV, which is in an excellent agreement with the position of the D-peak (cf. Fig 3(c)). An intermediate situation, Pu trilayer (3ML), demonstrates that increasing thickness leads to the band broadening, but also to a shift towards $E_F$. With a further increase of the Pu slab thickness up to five monolayers (5ML), the band broadening continues and the DOS becomes very similar to the bulk (cf. Fig. 3(a)). This broader 5$f$ band is in fact underlying the peak C, which explains why it is not observed. Moreover, the fact that in all four cases (bulk, 1, 3, and 5 monolayers) the non-magnetic state ($L = 0$, $S = 0$) persists, confirms the robustness of this solution.

It is also to mention that both LSDA and FLL-LDA+U magnetic solutions yield the DOS which does not correspond to the experimental UPS spectra shown in Fig. 3(c). In the LSDA case, the 5$f$-band has a very sharp peak structure in the region from $-1.2$ eV to 0.5 eV around $E_F$. For the FLL-LDA+U, the 5$f$-band becomes localized with the 5$f$ manifold well separated below the bottom of the valence band in the energy region from 2.5 to 4.5 eV below the $E_F$, again in a contradiction to experimental data.

To summarize, we have shown that the around-the-mean-field version of the LDA+U method yields non-magnetic ground state of $\delta$–Pu and, at the same time, it gives a good agreement with experimental data, namely, with the photoemission spectra, equilibrium volume, and bulk modulus. The fact that the non-magnetic character is not due to a mutual cancellation of spin and orbital parts of the moment, but is due to $S = 0$ and $L = 0$, is particularly corroborated by very recent neutron scattering experiments [5]. We are aware that our approach does not account for dynamical effects, which may become very important, as
suggested in Ref. [9]. Also, as we focused here on the magnetic, structural and spectroscopic properties of the \(\delta\)-Pu only, we do not discuss the \(\alpha\)– to \(\delta\)-Pu phase transition, leaving it for further consideration.

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