Electronic structure and non-magnetic character of $\delta$-Pu-Am alloys

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The around-mean-field LSDA+U correlated band theory is applied to investigate the electronic and magnetic structure of fcc-Pu-Am alloys. Despite a lattice expansion caused by the Am atoms, neither tendency to 5f localization nor formation of local magnetic moments on Pu atoms in Pu-Am alloys are found. The 5f-manifolds in the alloys are calculated being very similar to a simple weighted superposition of elemental Pu and Am 5f-states.

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Electron-electron correlation effects in a proximity to the localization threshold of the 5f series, which is crossed between Pu and Am, recently attracted significant attention in condensed matter physics $^1$. $^2$. $^3$. While strongly correlated systems usually have local magnetic moments, the whole set of experimental data clearly demonstrates their absence in Pu $^1$. Recent LSDA+U theoretical calculation $^4$ $^5$ have explained the non-magnetic character of $\delta$-Pu, leading to the 5f$^6$-like state, hybridized with conduction-electron states. An important issue remains open whether a further 5f localization or often speculated onset of magnetism can take place when expanding the lattice by Am doping.

Alloying Pu with Am provides an important opportunity to stabilize the high-temperature $\delta$-phase down to $T = 0$. Since Am atoms are larger than Pu, they create a “negative” pressure increasing the Pu interatomic spacing. Naively, knowing the sensitivity of the Pu phases to the lattice spacing, one can expect the formation of local magnetic moments at Pu due to an increase of 5f-states localization. In contrast, recent susceptibility measurements of the Pu-Am systems do not show any systematic variations and susceptibility remains very weakly temperature dependent, not exceeding $1 \times 10^{-8}$ m$^3$/mol $^7$. Also results of specific-heat studies $^8$ indicate no sign of magnetism in Pu-Am alloys.

The Pu-Am alloys were studied theoretically in Ref. $^9$, $^10$, using the local spin density (LSDA) and generalized gradient (GGA) approximations to the Density Functional theory (DFT), and no electron-electron correlations beyond those incorporated in LSDA/GGA were included. Large local magnetic moments on Pu and Am atoms in Pu-Am alloys (disordered or antiferromagnetically coupled) were calculated in Ref. $^9$, in contradiction to experimental findings $^{11}$ $^{12}$. The situation is similar to the DFT calculations (both within LSDA and GGA approximations) for elemental $\delta$-Pu $^{11}$ $^{12}$ and fcc-Am $^{11}$ $^{12}$, where magnetism tends to appear as an undesirable artifact.

In this Communication we go beyond the conventional LSDA/GGA approximations and apply the LSDA+U correlated energy-band approach to investigate the electronic structure of the Pu-Am alloys. The LSDA+U method $^{11}$ $^{12}$ starts from the LSDA total energy, which is supplemented by an additional intra-atomic Coulomb $U$ correlation term and an intraatomic exchange interaction $J$ term of multiband Hubbard-type minus a so-called double counting term, to subtract the electron-electron interaction already included in the LSDA. Our calculations are performed using the relativistic version of the “around-mean-field” LSDA + U method (AMF-LSDA+U) $^9$, as implemented in the full-potential linearized augmented-plane-wave (FP-LAPW) basis $^{10}$ in which the spin-orbit coupling (SOC) is taken into account $^{17}$.

Before considering in detail the effect of Coulomb correlations for the Pu-Am alloys, we need to make sure that the AMF-LSDA+U is capable to deal with the end-points, namely $\delta$-Pu and fcc-Am. Applied to $\delta$-Pu $^9$, this approach accounted for all basic characteristics: equilibrium volume, bulk modulus, 5f-manifold binding energy, including the disinclination to magnetic ordering, appearing due to a combined effect of SOC and Coulomb $U$, which lead to a nearly closed 5f$_{5/2}$ subshell, hybridized with conduction electron states. We note that the non-magnetic $\delta$-Pu can be obtained in fully-localized-limit (FLL)-LSDA+U calculations $^9$ when no spin-polarization is allowed in the LSDA part and unreasonably small value of the exchange $J < 0.48$ eV is used.

Here we focus on the issue how can the same method describe similar (in terms of the 5f occupancy), but presumably much more localized 5f-states in Am metal. We restricted ourselves to the fcc phase, which covers a broad concentration range from $\delta$-Pu nearly to pure Am $^{18}$. Also, it is the Am phase stable at elevated temperatures and at high pressure $^{19}$. The Am atom has six $f$ electrons with full $j = 5/2$ shell and zero magnetic moment. When the 5f states are treated as non-spin-polarized valence states in GGA, the calculated equilib-
TABLE I: Ground state properties of fcc-Am. Given are the 5f occupation number \( n_{5f} \), the spin moment \( M_s \), the orbital moment \( M_l \), and the total magnetic moment \( M_B \) (spin+orbital), and equilibrium volume \( V_{eq} \) and bulk modulus \( B \). The experimental value of \( B \), taken from Ref. 21, belongs to the dhcp structure.

| Method            | \( n_{5f} \) | \( M_s \) | \( \mu_B \) | \( M_l \) | \( \mu_B \) | \( V_{eq} \), a.u. | \( B \), GPa |
|-------------------|--------------|-----------|-----------|---------|-----------|----------------|------------|
| GGA+OP [12]       | N/A          | 6         | -1        | 5       | 170       | 43.0           |            |
| open-core         | 6            | 0         | 0         | 0       | 202       | 46.8           |            |
| open-core         | 6            | 0         | 0         | 0       | 180       | 46.0           |            |
| LSDA-SIC [23]     | 6            | 0         | 0         | 0       | 213       | 39.5           |            |
| LSDA+U=3 eV       | 5.92         | 0         | 0         | 0       | 182       | 67.3           |            |
| LSDA+U=4 eV       | 5.90         | 0         | 0         | 0       | 186       | 55.1           |            |
| Exp. [21]         | 6            | N/A       | N/A       | 0       | 198       | 29.9           |            |

When spin polarization is included in GGA calculations [12], augmented by well known orbital polarization correction [22] (GGA+OP), the \( V_{eq} = 170 \) (a.u.)\(^3\) improves significantly. However, large spin \( M_s = 6 \mu_B \) and orbital \( M_l = -1 \mu_B \) moments are induced at the Am atom. This strong magnetic state, either ordered or disordered, was never seen experimentally.

Another line to improve \( V_{eq} \) assumes the 5f-manifold to be a part of an atomic-core (the “open-core” approximation), and neglects an overlap between the 5f-states and the rest of valence electrons. It increases the volume to 180 [12] or 202 [20] (a.u.)\(^3\) in agreement with the experiment. While the “open-core” approximation is based on a very strong constraint and corresponds to a non-physical limit of infinitely large Coulomb repulsion in the f-shell, it illustrates the impact of the 5f-localization for Am. Alternatively, self-interaction correction (SIC) to LSDA can be employed to localize the 5f\(^6\) manifold. The LSDA-SIC yields the \( V_{eq} \) of 213 (a.u.)\(^3\) which is somewhat larger than experimental value. Similarly to the “open-core”, the LSDA-SIC gives a localized Am 5f\(^6\) shell. While being \( \textit{ab-initio} \) and working well at Am end, the LSDA-SIC strongly overestimates the localization in \( \delta\)-Pu yielding \( V_{eq} = 218 \) (a.u.)\(^3\) exceeding the experimental value by about 30 %. This illustrates the difficulty of LSDA-SIC method to deal with electron-electron correlations in \( \delta\)-Pu, which limits further the applicability of LSDA-SIC to Pu-Am alloys.

We performed AMF-LSDA+U calculations for Am, starting from the strongly spin-polarized LSDA charge and spin densities and on-site spin and orbital occupations, and without any constraints. We varied the Coulomb \( U \) from 3 eV to 4 eV, and chose the intra-atomic exchange parameter \( J = 0.75 \) eV, i.e. in the range of commonly accepted values for Am. The calculations converged to practically zero magnetic moment with residual \( M_s \) and \( M_l \) less than 0.01 \( \mu_B \), and 5f-manifold occupation \( n_{5f} = 5.9 \). Also, \( V_{eq} = 186 \) (a.u.)\(^3\) and bulk modulus \( B = 55.1 \) GPa are calculated for \( U = 4 \) eV, in a reasonable agreement (considering the different structure type) with experiment (see Table I).

In Fig. 1 (top) we show the total (TDOS) and f-states projected densities of states (fDOS) resulting from the fcc-Am LSDA and AMF-LSDA+U=4 eV calculations. The strong spin-polarization found in LSDA disappears in AMF-LSDA+U, resulting in a truly non-magnetic \( (S_z = L_z = J_z = 0) \) 5f\(^6\) ground state. The 5f manifold binding energy is calculated as \( \approx 3.5 \) eV (for \( U = 3 \) eV), 4 eV (\( U = 4 \) eV). The LSDA+U method is not based on any kind of atomic coupling scheme (\( L_S \) or \( jj \)), it rather determines the set of single-particle orbitals that minimize variationally the total energy. The AMF-LSDA+U result can be interpreted as yielding the \( J = 0 \) singlet ground-state configuration that corresponds to the \( jj \)-coupled Slater determinant formed of fully and equally populated six \( j = 5/2 \) orbitals.

Although the DOS cannot be directly compared with 5f features in valence-band photoelectron spectra (PES), as - for localized 5f states - those reflect not the 5f\(^n\) ground state, but the whole 5f\(^n-1\) multiplet, the energy range is undoubtedly correct [24 25]. Comparing to results of Pu calculations (see Fig. 3 of Ref. [23]), the Am 5f states are not only at higher binding energy, but also
conspicuously narrower, with the width not exceeding 0.1 eV. The results obtained for Am at ambient pressure can be definitely characterized as 5f-localized. Shift of the 5f states in AMF-LSDA+U down from the vicinity of the Fermi energy ($E_F$) decreases their contribution to the chemical bonding and increases $V_{eq}$.

The situation of the 5f states changes dramatically when the volume is reduced from 198 (a.u.)$^3$ to 133 (a.u.)$^3$, which corresponds to the volume of the high pressure phase AmIV. This phase is generally assumed, as the orthorhombic structure reminiscent of α-U, to have itinerant 5f states [12]. Indeed, our calculations exhibit the 5$f_{5/2}$ band broadened nearly up to 1 eV. The width of the 5$f_{5/2}$ band becomes thus comparable to δ-Pu, although there remains a large difference in binding energies: in δ-Pu, the 5$f_{5/2}$ band is located around 1 eV below $E_F$, while in Am it is centered at 3.5 eV even for the high-pressure phase, just below the lower edge of the valence band.

Next, we turn to the salient aspect of our investigation, the AMF-LSDA+U calculations of Pu$_x$Am$_{1-x}$ ($x = 0.25, 0.5, 0.75$) alloys. In all calculations, the Coulomb $U = 4$ eV, and exchange $J = 0.75$ eV for Am atom, and $U=4$ eV, $J=0.70$ eV for Pu atom were used. The fcc-based super-cells were used, $L_{12}$ for Pu$_3$Am ($Pu_{0.75}Am_{0.25}$) and PuAm$_3$ ($Pu_{0.25}Am_{0.75}$), and $L_{10}$ for PuAm ($Pu_{0.5}Am_{0.5}$). The lattice parameters, 8.905 (a.u.)$^3$ for $Pu_{0.75}Am_{0.25}$, 9.018 (a.u.)$^3$ for $Pu_{0.25}Am_{0.75}$, and 9.132 (a.u.)$^3$ for $Pu_{0.25}Am_{0.75}$, were taken from Ref. [18].

The LSDA calculations produce magnetic solutions for all considered Pu-Am alloys, similar to those reported in Ref. [3]. Starting from these spin-polarized LSDA charge and spin densities and on-site spin and orbital occupations, we apply AMF-LSDA+U. The magnetism collapses in all cases, and Pu-Am alloys become non-magnetic, similarly to fcc-Am and δ-Pu. The calculated DOS (total per unit cell and 5f-projected (fDOS)) are shown in Fig.1 (bottom) for $Pu_{0.75}Am_{0.25}$ (PuAm) alloy. The Am 5f-manifold is located at ~4 eV below $E_F$, similarly to AMF-LSDA+U DOS for fcc-Am (see Fig. 1(top)). The Pu-5f states are located in a region from ~2 eV to 0.5 eV and peaked at ~1 eV below $E_F$, similarly to the DOS of δ-Pu shown in Fig. 3 of Ref. [3] (one also should keep in mind that there are small DOS changes due to the change in the lattice parameter). Importantly, the alloy DOS is almost exactly a weighted superposition of pure fcc-Am and δ-Pu DOS showing that there is a very little interaction between Am- and Pu-5f manifolds. The calculated DOS for $Pu_{0.5}Am_{0.5}$ and $Pu_{0.25}Am_{0.75}$ look qualitatively very similar to $Pu_{0.75}Am_{0.25}$ DOS shown in Fig. 1 (bottom), with well separated Am and Pu 5f-manifolds, whose relative heights are proportional to the Am and Pu atom concentration, again supporting the smallness of the interaction between the Am- and Pu-5f states. The difference between equilibrium volumes of δ-Pu and fcc-Am is relatively small (~15 %) and no significant deviation from Vegard’s law is found in experiment [18]. Considering the lattice compression with a decrease of Am content, we did not find any sizeable effect on Am-5f states. The lattice compression is simply too small compared to the changes at high pressure, and Am remains still practically in the AmI phase, i.e. below the first phase transition at 6 GPa. Similarly, there is no significant change in Pu-5f states found with a decrease of Am content, just a small (~0.2 eV) decrease in the binding energy. It is also noteworthy that we did not find any sizable change in the Pu-5f and Am-5f manifold occupations ($n_{5f}$) [26].

In Fig.2 we show the valence-band PES of δ-Pu, Am, and $Pu_{0.67}Am_{0.33}$, obtained with the photoexcitation energy 40.81 eV, emphasizing the emission from the 5f states. Although in the case of band systems PES provides practically a snapshot of the density of one-electron states, final-state effects are important for localized as well as narrow-band systems. In analogy to rare-earths, the valence-band spectrum of Am should exhibit the multiplet of excited states. To address these effects, the one-particle Green’s function and corresponding spectral density were calculated for Am atom. In these calculations we used exact diagonalization of the many-body hamiltonian for $f^n$-shell closely following Ref. [28], adding the SOC ($\xi = \frac{0.33}{1}$ eV), and using the values $U = 4$ eV and $J = 0.75$ eV, as in the AMF-LSDA+U calculations. Also, $k_B T = 0.1$ eV and $\langle N_f \rangle = 6$ were used to determine the...
chemical potential ($E_F$). The calculated spectral density shown in Fig. 2 (Am - photoexcitations) and agrees very well with similar recent calculations of Svane [28]. It is in a conspicuously good agreement with experimental PE spectra. Such comparison cannot be done in the case of Pu, as the use of the atomic limit for the Pu 5f states is not justified. The Am-$f^6$ many-body ground state is found to have $J = 0$ character with both $S = L = 2.471$, while neither $S$ nor $L$ is a good quantum number. It differs from the the result of Ref. 31 that yields LS-coupled $^7F_g$ ground state.

Although the experimental PES cannot be accounted for by the LSDA+U theory, one can see that the calculated spectrum of the Pu-Am alloy corresponds to the weighted average of spectra of pure Pu and Am, similarly to the PE spectra. As shown recently [27], the Pu-$4f$ spectra of Pu-Am alloys remain practically identical irrespective of Am concentration at least up to $\approx 35 \%$ Am. Also, very recent results of specific-heat studies [8] indicate no enhancement of the $\gamma$ coefficient of the electronic specific heat. We can conclude that the lattice expansion caused by Am is not driving the Pu 5f states to further localization and no magnetic moments on Pu in $\delta$-Pu-Am alloys are induced thereby. Both from the experiment and theory, we deduce that the character of the Pu-5f states does not change with the Am doping. The experimental PES features close to $E_F$ can not be explained in terms of simple band states, similarly to the case of $\delta$-Pu for which the dynamical effects become very important [1].

To summarize, we demonstrated that the around-mean-field version of the LSDA+U method gives a unified picture of the electronic structure of Am, $\delta$-Pu and $\delta$-Pu-Am alloys. For $fcc$-Pu-Am our calculations yield a non-magnetic ground state which is almost exactly a localized $^6f^0 J = 0$ singlet state, with equilibrium volume and bulk modulus in a good agreement with experimental data. Based on the calculations, we expect that this non-magnetic state will be preserved even for the pressure-delocalized state of Am, in accord with electrical resistivity lacking any clear anomaly of magnetic origin.

Neither magnetism nor further localization of the Pu-5f states is found in $fcc$ Pu-Am alloys on the LSDA+U level, i.e. without introducing any additional effects like magnetic moment disorder or magnetic fluctuations, which are disproved recently by $\mu$SR experiments [31]. We are aware that our static mean-field approach does not account for a possible Kondo screening of the magnetic moment fluctuations, which are important in other f-electron systems (e.g. $\alpha$-Ce).

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