Electronic structure and magnetic state of transuranium metals under pressure

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Received 13 August 2010, in final form 30 September 2010
Published 19 November 2010
Online at stacks.iop.org/JPhysCM/22/495501

Abstract

The electronic structures of bcc Np, fcc Pu, Am, and Cm pure metals under pressure have been investigated employing the LDA + U method with spin–orbit coupling (LDA + U + SO). The magnetic state of the actinide ions was analyzed in both LS and jj coupling schemes to reveal the applicability of corresponding coupling bases. It was demonstrated that whereas Pu and Am are well described within the jj coupling scheme, Np and Cm can be described appropriately neither in a \(\{m\sigma\}\), nor in a \(\{jm\}\) basis, due to intermediate coupling scheme realization in these metals that requires some finer treatment. The LDA + U + SO results for the considered transuranium metals reveal band broadening and gradual 5f electron delocalization under pressure.

(Some figures in this article are in colour only in the electronic version)
the exchange interaction was found to be the reason for the artificial antiferromagnetic ordering in various LSDA + U investigations. Also the nonmagnetic ground state was found in the around-mean-field version of the LDA + U method [11], and later on within the LDA + Hubbard I approximation [12], and also hybrid density functionals with a dominant contribution of the HF functional [13]. Recently, the reliability of these results was supported by more detailed analysis of exchange interaction [14], and also in the LDA + DMFT calculations [15], supplementing LDA with the dynamical mean-field theory [16] (DMFT) [17–20].

While a consistent interpretation of spectroscopic data has not been found yet [21], the LDA + U + SO method provides a realistic magnetic state and allows one to estimate the electrical resistivity in actinide metals [22] and alloys [23] in good agreement with experimental data.

In this paper the electronic structure of bcc Np, fcc Pu, Am, and Cm pure metals was calculated within the LDA + U + SO method introduced in detail in [10]. In the method the exchange interaction (spin-polarization) term in the Hamiltonian is implemented in a general nondiagonal matrix form regarding the spin variables. This form is necessary for the correct description of the 5f electrons’ behavior for the cases of jj and intermediate coupling types [10].

In the LDA + U + SO method [10] accounting for strong electron correlations includes Coulomb interaction matrix elements which can be expressed via direct U and exchange \( J_H \) Coulomb parameters. A reliable way to estimate these parameters is provided by the constrain LDA approach [24]. To calculate a value of the U parameter, in this procedure one evaluates a screened Coulomb interaction of 5f electrons which requires the choice of screening channels to be taken into account. For the s, p, and d channels for bcc Np and fcc Pu, Am, and Cm the constrain LDA calculations resulted in the Coulomb parameter value \( U = 4 \) eV [10, 17]. The exchange Coulomb parameter \( J_H \) is evaluated as the difference of interaction energy for the electron pairs with the opposite and the same spin directions. Parameter \( J_H \) does not depend on the screening channel choice. For neptunium and plutonium, the value of Hund exchange parameter \( J_H \) was calculated as \( J_H = 0.48 \) eV [10], for americium as 0.49 eV, and for curium as 0.52 eV [22]. In this work in all LDA + U + SO calculations we used these exact values of \( J_H \) for each actinide metal, since the (non)magnetic state of actinide metals is sensitive to the value of \( J_H \) [10].

The strong spin–orbit coupling of 5f electrons results in a splitting of the f band into subbands corresponding to the values of total moment \( j = 5/2 \) and \( 7/2 \). The value of this splitting is 1–1.5 eV. Taking into account Coulomb correlations via the LDA + U correction does not qualitatively change the band structure, only the separation between subbands increases from 1.5 to 5 eV according to the value of \( U = 4 \) eV.

The density of states (DOS) from the LDA + U + SO calculations for Np, Pu, Am, and Cm at ambient pressure are shown in figure 1. In all DOS one can distinguish two groups of bands: \( j = 5/2 \) at the lower energies and \( j = 7/2 \) at higher ones. In Np the \( j = 5/2 \) subband is partially filled. From Pu to Cm the Fermi level is shifted upward from the upper slope of the \( j = 5/2 \) subband in Pu and crosses the \( j = 7/2 \) subband in Cm due to the increasing number of f electrons. These results are for the metals at ambient pressure in the cubic phases. We used the same lattice parameters as in our previous work [23].

To model the pressure, we assume it to be uniform and applied as a cell volume contraction. While experimentally the crystal structure of these metals transforms from cubic to complicated structures like orthorhombic and monoclinic, for the electronic structure and magnetic state of the actinide ion the main result of the applied pressure comes from the contraction of the unit cell volume per ion. In figures 2–5 one can find the density of states (DOS) for the cubic phases under pressure; real phases with corresponding volumes per ion are referred to in brackets. In some metals under investigation the cubic phases do not correspond to the largest volume per ion; for this reason we also consider some volumes exceeding the cubic volume at ambient pressure.

**Neptunium metal.** The magnetic ground state for Np at ambient pressure was found in our calculation (see table 1). The large values of the off-diagonal elements (OD) in table 1 in both the \([m\sigma]\) and \(jm_l\) bases show evidence for the intermediate coupling type in this actinide metal. The four largest eigenvalues close to the unit give the \( \mathbf{t}^6 \) configuration. Upon applied pressure the density of states at the Fermi energy increases, see figure 2, the effective magnetic moment \( \mu_{\text{eff}} \) ranges from 2.55 to 2.33 \( \mu_B \).
Table 1. Electronic configuration of the 5f shell in Np, Pu, Am, and Cm ions in the cubic phases calculated within the LDA + U + SO method. The largest values of the occupation matrices’ off-diagonal elements OD$_{LS}$ and OD$_{jm}$ in the corresponding basis sets are given in the second and third columns. Then the seven largest eigenvalues of the occupation matrix are presented. The columns from the eleventh to thirteenth show the calculated values for spin (S), orbital (L), total (J) moments.

| Metal | OD$_{LS}$ | OD$_{jm}$ | Largest eigenvalues |
|-------|-----------|-----------|---------------------|
| Np    | 0.36      | 0.46      | 0.26 0.89 0.91 0.92 1.40 4.68 3.28 |
| Pu    | 0.45      | 0.01      | 0.93 0.93 0.93 0.93 0.0 0 0 |
| Am    | 0.47      | 0.02      | 0.98 0.98 0.99 0.99 0 0 0 |
| Cm    | 0.31      | 0.45      | 0.99 0.99 0.99 0.99 2.77 0.75 3.52 |

Figure 2. The partial DOS for the $j = 5/2$ (shaded area) and $j = 7/2$ (dashed line) subbands of bcc neptunium under pressure obtained from the LDA + U + SO calculations. For each curve the relative volume $V/V_0$ is given. Fermi energy corresponds to zero.

Plutonium metal. The LDA + U + SO calculations for the metallic Pu fcc structure (the fcc phase in Pu is named the $\delta$-phase) at all volumes gave a nonmagnetic ground state with zero values of spin S, orbital L, and total J moments [10] in agreement with numerous experimental data [9]. The occupation matrix has six eigenvalues close to the unit, see table 1 (for details, see [10]), and is nearly diagonal in the ($jm_j$) basis of the eigenfunctions of the total moment $J$. This gives a f$^6$ configuration of the Pu ion in the $jj$ coupling scheme. In figure 3 the partial densities of states for the $f^{5/2}$ and $f^{7/2}$ subshell of Pu in all volumes (applied pressures) are presented. The DOS as well as the occupation matrix demonstrate an almost completely filled $f^{5/2}$ band with the Fermi level on the top of it and an empty $f^{7/2}$ band. The separation between the centers of these bands is $\approx 5.2$–$5.4$ eV. For small volumes the $j = 5/2$ subband does not change its position but its bandwidth becomes approx. 1 eV larger. Further calculations employing the LDA + DMFT method should correct the intensities of peaks in better agreement with the available spectroscopic data [18].

Americium metal. The calculated DOS of Am are shown in figure 4. One can see that the $j = 5/2$ subband is fully occupied which corresponds to a f$^6$ configuration whereas the $j = 7/2$ subband is almost empty. The occupation matrix has six largest eigenvalues of close to unit, see table 1. The Fermi level in Am is shifted towards the $j = 7/2$ subband comparing to Pu due to an additional valence electron (see figure 4) that occupies the s, p, and d states (not shown separately). Note, that the 5f bandwidth in Am is smaller than in Pu due to the larger cell volume per ion. Having a delicate balance between SO and exchange interactions, the calculated 5f-DOS occupied 5f band is centered around 4 eV in agreement with Am photoemission spectra that demonstrate large density of states in the range ($−4; −2$ eV) [25]. The LDA+U+SO calculations for Am gave a nonmagnetic ground state in all volumes of $S = L = J = 0$ in agreement with experimental data [2]. For all volumes of Am we obtained an f$^6$ electronic configuration while in the LDA + DMFT (Hubbard I) calculations [26] under pressure transitions to the f$^7$ configuration were calculated. In LDA + U+SO such transitions are not included due to the static mean-field approach used.
Curium metal. In curium the $f^{7/2}$ subband is partially filled, providing a peculiar empty state well below the Fermi level, see Figure 5. The LDA + U + SO calculation results in the $S$ and $L$ moments listed in Table 1. The value of the effective magnetic moment $μ_{\text{eff}}$ calculated from the total moment value $J$ by the method used in [10] for different volumes gradually decreases from 7.44 $μ_B$ for the largest volume (corresponding to the volume per ion in the CmI phase) to 6.86 $μ_B$ (CmIV). This result corresponds to the model calculations assuming in pure LS coupling the magnetic moment of the curium ion to be 7.94 $μ_B$, but for a realistic model of intermediate coupling lowering up to 7.6 $μ_B$ [27], while experimentally the magnetic moment was reported as 7.85 $μ_B$ [27].

Conclusion

We have calculated the electronic structure of bcc Np, fcc Pu, Am, and Cm pure metals within the LDA + U + SO method under applied pressure in the assumption of uniform unit cell contraction. The static mean-field approach used in this work results in gradual (featureless) electron delocalization and band broadening under pressure, without abrupt changes corresponding to structural transition. While the $jj$ coupling scheme is well suited for the description of the Pu and Am ground states, for Np metal only the intermediate coupling scheme seems to be appropriate, whereas in Cm the intermediate coupling is closer to the $LS$-type. We suggest that accounting for dynamical correlations effects will allow one to reproduce not only the delocalization of 5f electrons under applied pressure but also will resolve some fine features of this process.

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