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Magnetic state and electronic structure of the δ and α phases of metallic Pu and its compounds

A. O. Shorikov,[1] A. V. Lukoyanov,[1,2] M. A. Korotin,[1] and V. I. Anisimov[1]
[1]*Institute of Metal Physics, Russian Academy of Sciences—Ural Division, 620041 Yekaterinburg GSP-170, Russia*
[2]*Ural State Technical University—UPI, 620002 Yekaterinburg, Russia*

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By the local density approximation with on-site Coulomb repulsion U (LDA+U) method with spin-orbit coupling (LDA+U+SO) the magnetic state and electronic structure have been investigated for plutonium in δ and α phases and for the Pu compounds PuN, PuCoGa$_5$, PuRh$_2$, PuSi$_2$, PuTe, and PuSb. In agreement with experiment we found for metallic plutonium in both phases a nonmagnetic ground state with Pu ions in f^6 configuration with zero values of spin, orbital, and total moments. This result is determined by a strong spin-orbit coupling in the 5f shell. It leads to the clear splitting of 5f states into $f^{5/2}$ and $f^{7/2}$ subbands even in the LDA calculation. The Fermi level is in a pseudogap between them, so that the $f^{5/2}$ subshell is already almost completely filled with six electrons before Coulomb correlation effects are taken into account. The competition between spin-orbit coupling and the exchange (Hund) interaction (favoring a magnetic ground state) in the 5f shell is so delicately balanced that a small increase (less than 15%) of the exchange interaction parameter value from J_H=0.48 eV obtained in the constrained LDA calculation would result in a magnetic ground state with nonzero spin and orbital moment values. For the Pu compounds investigated in the present work, a predominantly f^6 configuration with nonzero magnetic moments was found in PuCoGa$_5$, PuSi$_2$, and PuTe, while PuN, PuRh$_2$, and PuSb have the f^5 configuration with sizable magnetic moment values. Whereas the pure jj coupling scheme was found to be valid for metallic plutonium, an intermediate coupling scheme is needed to describe the 5f shell in Pu compounds. The results of our calculations show that the exchange interaction term in the Hamiltonian should be treated in a general matrix form for Pu and its compounds.

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I. INTRODUCTION

In actinide elements the Coulomb interaction of the 5f electrons is of the same order as the bandwidth and spin-orbit coupling. Their interplay results in the complicated physics of 5f compounds[1] where both theorists and experimentalists still have plenty of work. Among the actinides, the element plutonium seems to be the most intriguing,[2,3] despite numerous works and the 60 years passed since the Pu discovery.[4,5]

The electronic properties of plutonium show an exceptional example of a system with 5f electrons on the edge between localization and itinerancy.[3,6] Experimental work[7] gave jj coupling for Pu 5f electrons or an intermediate coupling close to jj type.[8] A theoretical model for the intermediate coupling scheme was suggested for PuSb by Cooper *et al.*[9]

Many experiments have been carried out to shed light on plutonium electronic structure. For δ-plutonium, the most investigated of all metallic Pu phases, photoemission spectroscopy (PES) revealed special features of the valence band,[10–12] in particular, a sharp peak at the Fermi level. X-ray, high-resolution ultraviolet,[13] and resonant photoemission[14] spectroscopy measurements accompanied by Pu 4f core-level spectra show a more localized character of the 5f electrons in the δ-Pu phase compared with the α phase. The sharp peak at the Fermi level is indicative of a strong many-particle nature and heavy-fermion behavior of 5f electrons. The electron mass enhancement is usually characterized by the inferred Sommerfeld coefficient γ =50 mJ mol^{-1} K^{-2} for δ-Pu,[15] versus γ=17 mJ mol^{-1} K^{-2} for α-Pu.[16] The phonon dispersions and elastic moduli of δ-Pu show a number of anomalies,[17,18] including softening of the transverse [111] modes,[19] suggesting an unusual electronic structure and phonon-electron interaction for the 5f electrons in plutonium (modern calculation results[20] qualitatively predicted the experimental data). No evidence for ordered or disordered magnetic moments in plutonium in either δ or α phase is found in experiments.[2,4,21]

Ab initio calculations of the electronic structure for plutonium have been done by many authors.[22] The standard local density approximation[23] (LDA) as well as the generalized gradient approximation[24] (GGA) have been implemented. The full-potential linearized augmented plane-wave (FLAPW) method with GGA correction and Gaussian-type-orbital fitting function (LCGTO-FF) methods were used to reproduce the zero-pressure experimental volumes and bulk modulus of Pu in the row of all actinides.[25] The obtained results show better agreement with the experiment than, for example, the linear muffin-tin-orbitals (LMTO) GGA method[26] but fail when used with Pu. Even with the proper second-variational approach to 6p states,[27] the experimental volume of δ-Pu is still unattainable.[28] Another limitation of all these methods, as was realized later, is the inability to reproduce correctly the electronic structure of plutonium due to neglect of Coulomb correlation effects.

To improve the LDA approximation the LDA+U method[29] was used, which explicitly takes into account the strong Coulomb repulsion between 5f electrons by adding a Hubbard-like term to the LDA Hamiltonian. The calculation of the electronic structure for fcc Pu by the LDA+U method with GGA correction was performed in Ref. 30. The authors showed that for the standard set of Slater integrals[31,32] and Coulomb parameter U=4.0 eV the calculated value of the

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equilibrium volume agrees better with the experimental data. The resulting band structure suggests that Pu has five localized f electrons with substantial orbital and spin moment values. Another local spin density approximation with on-site Coulomb repulsion U (LSDA+U) calculation with GGA correction gave similar results for different Coulomb parameter values.[33]

In contrast to the experimental data, which clearly show a nonmagnetic state of plutonium,[2,4,21] an antiferromagnetic ground state was found for fcc Pu in many calculations.[34–37] A fully relativistic spin-polarized calculation for the fcc plutonium phase was performed in Ref. 38. In another work (Ref. 39) it was shown that "switching off" the hybridization leads to better agreement with experiment for the equilibrium volume in δ-Pu. For the augmented plane-wave basis (FLAPW),[40] Kutepov *et al.*[41] using the fully relativistic spin-polarized method with GGA approximation obtained large orbital and spin moments. An antiferromagnetic ordered state was found to be lower in the total energy of the system compared with a nonmagnetic one for both α- and δ-Pu phases.[41,42]

Another scheme was proposed by Eriksson *et al.*[43] The plutonium $5f$ electrons were divided into localized and delocalized ones. The self-interaction correction (SIC) LSDA method[44–47] was used to calculate volumes and total energies of the Pu ion in different configurations (with different valencies[44,48]). In contrast to experiments,[7] an *LS*-coupled ground state was found to be lower in the total energy for any configuration of the Pu ion[48] and the f^3 was configuration energetically preferable. For many binary Pu compounds the SIC LSDA calculations showed that the experimental data are better described by the model of coexisting localized and delocalized electrons.[49] In particular, by the same approach a valency +5 was found for the Pu ion in PuN and +3 in PuTe and PuSb.[49] The Pu ion in plutonium dioxide was obtained in the f^4 configuration.[48,50] A similar hybrid scheme, the disordered local moment method,[51] gave qualitative agreement with the photoemission spectrum for δ-Pu.[52]

Experiments suggest the presence of significant correlation effects for $5f$ electrons in plutonium. Dynamical mean-field theory[53–55] (DMFT) is a powerful tool in studying such effects. Merging of the LDA-based methods with DMFT gave a new calculation scheme—the LDA+DMFT method.[56–58] Its application to the plutonium problem[58,59] gave a better agreement with photoemission experiments and a double-minimum curve of the total energy as a function of volume.

In this paper we present the results of calculations by the LDA+U with spin-orbit coupling (LDA+U+SO) method of the electronic structure and magnetic properties for metallic plutonium in the α and δ phases and a series of Pu compounds, namely, PuN, $PuCoGa_5$, $PuRh_2$, $PuSi_2$, PuTe, and PuSb. The exchange interaction (spin-polarization) term in the Hamiltonian was implemented in a general nondiagonal matrix form. This form is necessary for the correct description of $5f$ electrons for the case of jj coupling and intermediate coupling schemes which we have found to be valid in pure metallic Pu and its compounds. For metallic Pu in both δ and α phases, our calculations gave a nonmagnetic f^6 ground state with six f electrons in the fully occupied $j=5/2$ subshell and spin, orbital, and total moment values equal to zero. This result is in agreement with experimental data for metallic plutonium,[21] but we have found a magnetic ground state for all Pu-based compounds investigated in this work. For the present investigation we have chosen plutonium compounds with formal Pu ion valency +3 (PuN and PuSb) and +2 (PuTe) and also intermetallic compounds where the valence state of Pu ion is not obviously defined. All calculated Pu compounds have magnetic moments on Pu ions with f^5, f^6, or mixed configurations. In our work we were considering a magnetic state problem. Reference to equilibrium volume and volume transition can be found in other papers.[60] A strong competition between spin-orbit coupling and exchange interactions with a delicate balance was found to determine the magnetic state of Pu and its compounds.

The organization of this paper is as follows. Section II describes the LDA+U+SO method used in the present work. In Sec. III results of calculations for metallic δ- and α-Pu phases are discussed in detail. Then Sec. IV describes applications of the LDA+U+SO method to various plutonium compounds, including PuN in Sec. IV A, $PuCoGa_5$ in Sec. IV B, $PuRh_2$ in Sec. IV C, $PuSi_2$ in Sec. IV D, PuTe in Sec. IV E, and PuSb in Sec. IV F. Section V summarizes the paper.

II. METHOD

The strong spin-orbit coupling in actinides together with magnetism and Coulomb interactions cause a problem that is not present for materials without $5f$ electrons. For $3d$- and $4f$-element compounds, relatively weak spin-orbit coupling results in a Russell-Saunders coupling (*LS* coupling) scheme with **S** and **L** operators well defined. Then the basis of *LS* orbitals, which are eigenfunctions of both spin **S** and orbital **L** moment operators, is a good choice. In this case it is possible to define the quantization axis in the direction of the spin moment vector so that the occupation and potential matrices will be diagonal in the spin variables. When the spin-orbit coupling is stronger than the exchange (Hund) interaction, the jj coupling scheme is valid with a well-defined total moment **J**, but not spin **S** and orbital **L** moments. In this case, the basis $\{jm_j\}$ of the total moment operator eigenfunctions is the best choice. The matrix of the spin-orbit coupling operator is diagonal in this basis but not the exchange interaction (spin-polarization) term in the Hamiltonian.

The situation for $5f$ electrons is more complicated. The strengths of spin-orbit coupling and exchange interaction are comparable so that both aforementioned limits—*LS* coupling and jj coupling schemes—are not valid and an intermediate coupling scheme is needed to describe the $5f$ shell in actinides. In this case the occupation matrix is diagonal neither in $\{LS\}$ nor in $\{jm_j\}$ orbital bases and both terms in the Hamiltonian—spin-orbit coupling and exchange interaction—should be taken in a general nondiagonal matrix form.

In the LDA+U method[29] the energy functional E_{LDA+U} depends on the charge density $\rho(\mathbf{r})$ and the occupation matrix $n^{ss'}_{mm'}$. In our case it is the $5f$ occupation matrix because correlation effects are taken into account for $5f$ plutonium orbitals. The LDA+U method in a general form nondiagonal in spin variables was defined in Ref. 61:

$$E_{LDA+U}[\rho(\mathbf{r}),\{n\}] = E_{LDA}[\rho(\mathbf{r})] + E_U[\{n\}] - E_{dc}[\{n\}], \quad (1)$$

where $\rho(\mathbf{r})$ is the charge density and $E_{LDA}[\rho(\mathbf{r})]$ is the standard LDA functional. The occupation matrix is defined as

$$n^{ss'}_{mm'} = -\frac{1}{\pi}\int^{E_F} \mathrm{Im}\, G^{ss'}_{mm'}(E)dE \quad (2)$$

where $G^{ss'}_{mm'}(E)=\langle ms|(E-\hat{H}_{LDA+U})^{-1}|m's'\rangle$ are the elements of the Green's function matrix in the local orbital basis set (m is the magnetic quantum number and s the spin index for the correlated orbital). In the present work this basis set was formed of LMT orbitals from the tight-binding LMTO method based on the atomic-spheres approximation (TB-LMTO-ASA).[62] In Eq. (1) the Coulomb interaction energy $E_U[\{n\}]$ term is a function of the occupation matrix $n^{ss'}_{mm'}$,

$$E_U[\{n\}] = \frac{1}{2}\sum_{\{m\},ss'} \{\langle m,m''|V_{ee}|m',m'''\rangle n^{ss}_{mm'} n^{s's'}_{m''m'''} - \langle m,m''|V_{ee}|m''',m'\rangle n^{ss'}_{mm'} n^{s's}_{m''m'''}\} \quad (3)$$

where V_{ee} is the screened Coulomb interaction between the correlated electrons. Finally, the last term in Eq. (1) correcting for double counting is a function of the total number of electrons, in the spirit of the LDA which is a functional of total charge density

$$E_{dc}[\{n\}] = \frac{1}{2}UN(N-1) - \frac{1}{4}J_H N(N-2), \quad (4)$$

where $N=\mathrm{Tr}(n^{ss'}_{mm'})$ is the total number of electrons in the particular shell. U and J_H are the screened Coulomb and Hund exchange parameters which can be determined in the constrained LDA calculations.[63,64] The screened Coulomb interaction matrix elements $\langle m,m''|V_{ee}|m',m'''\rangle$ can be expressed via parameters U and J_H (see Ref. 29).

The functional Eq. (1) defines the effective single-particle Hamiltonian with an orbital-dependent potential added to the usual LDA potential,

$$\hat{H}_{LDA+U} = \hat{H}_{LDA} + \sum_{ms,m's'} |ms\rangle V^{ss'}_{mm'}\langle m's'|, \quad (5)$$

$$\begin{aligned} V^{ss'}_{mm'} = {} & \delta_{ss'}\sum_{m'',m'''} \{\langle m,m''|V_{ee}|m',m'''\rangle n^{-s,-s}_{m''m'''} \\ & + (\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle) n^{ss}_{m''m'''}\} \\ & - (1-\delta_{ss'})\sum_{m'',m'''} \langle m,m''|V_{ee}|m''',m'\rangle n^{s's}_{m''m'''} \\ & - U\left(N-\frac{1}{2}\right) + \frac{1}{2}J_H(N-1). \end{aligned} \quad (6)$$

In this paper we used the method abbreviated as LDA+U+SO which comprises the LDA+U Hamiltonian Eq. (6), nondiagonal in spin variables, with spin-orbit coupling term,

$$\hat{H}_{LDA+U+SO} = \hat{H}_{LDA+U} + \hat{H}_{SO},$$

$$\hat{H}_{SO} = \lambda \mathbf{L}\cdot\mathbf{S}, \quad (7)$$

where λ is the parameter of spin-orbit coupling. In the LS basis the SO coupling matrix has nonzero matrix elements both diagonal $(H_{SO})^{s,s}_{m',m}$ and off diagonal $(H_{SO})^{\uparrow,\downarrow}_{m',m}$ and $(H_{SO})^{\downarrow,\uparrow}_{m',m}$ in spin variables (in complex spherical harmonics)[65]

$$(H_{SO})^{\uparrow,\downarrow}_{m',m} = \frac{\lambda}{2}\sqrt{(l+m)(l-m+1)}(\delta_{m',m-1}),$$

$$(H_{SO})^{\downarrow,\uparrow}_{m',m} = \frac{\lambda}{2}\sqrt{(l+m)(l-m+1)}(\delta_{m'-1,m}),$$

$$(H_{SO})^{s,s}_{m',m} = \lambda ms\,\delta_{m',m}, \quad (8)$$

where lm are the orbital quantum numbers, and the spin index $s=+1/2,-1/2$.

These formulas are written in the $\{LS\}$ basis set. The LDA+U+SO formalism described above is invariant to the unitary transformation of the orbital basis set. In the case of $5f$ elements the $\{jm_j\}$ basis of eigenfunctions of total moment $\mathbf{J}$ is appropriate for the description of the jj coupling type. In our work all calculations were performed in the $\{LS\}$ basis set; then the resulting Green's function matrix Eq. (2), if necessary, was transformed into the $\{jm_j\}$ basis using standard formulas.

The exchange interaction is originally a part of the Coulomb interaction [the second term in Eq. (3)]. In the case when the spin moment operator $\mathbf{S}$ is well defined, so that density and potential matrices can be made diagonal in spin variables, it is convenient to define the spin-polarized density and spin-polarized potential. In the most general form the exchange interaction allowing noncollinearity of the spin polarization was introduced in density functional theory[66] (DFT) by von Barth *et al.*[67,68] and used later in Refs. 69 and 70,

$$\left[\left(-\nabla^2 + V_{ext}(r) + \int d^3r'\rho(r')\frac{e^2}{|r-r'|} + v_{xc}(r;\rho,\vec{m})\right)\sigma_0 + \vec{b}_{xc}(r;\rho,\vec{m})\cdot\vec{\sigma}\right]\Psi_i(r) = \varepsilon_i\Psi_i(r) \quad (9)$$

where $\Psi_i(r)$ are one-electron spinors, σ_i are Pauli matrices, $V_{ext}(r)$ is the external potential, and ε_i are eigenvalues. The exchange-correlation potentials determined as variational derivatives over space charge density $\rho(r)$ or magnetization vector $\vec{m}(r)$ are

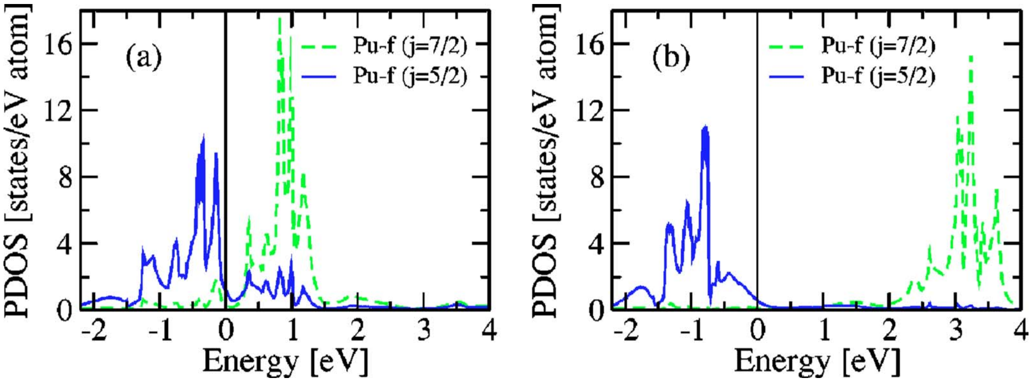

FIG. 1. (Color online) Partial $f^{5/2}$ and $f^{7/2}$ contributions to $5f$ band densities of states of δ-plutonium calculated with the LDA (a) and LDA+U+SO (b) method.

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho,\vec{m}]}{\delta\rho(r)}, \quad \vec{b}_{xc}(r) = \frac{\delta E_{xc}[\rho,\vec{m}]}{\delta\vec{m}(r)} = \frac{\delta E_{xc}[\rho,m]}{\delta m}\hat{m}(r). \tag{10}$$

The exchange interaction is described here by the local magnetic field $\vec{b}_{xc}$ which acts on all orbitals in the same way. The potential matrix in the *LS* basis for this field is diagonal in spin variables if the quantization axis is chosen along the direction of $\vec{b}_{xc}$.

A strong spin-orbit coupling in the $5f$ shell produces an occupation matrix Eq. (2) and the corresponding potential matrix Eq. (6) which cannot be made diagonal in spin variables by rotation of the quantization axis. Such a rotation should be done in the direction of the spin moment vector, so that only S_z components were present, while the S_x and S_y components (responsible for terms in the Hamiltonian off diagonal in the spin variable) were set to zero. This is possible in the case where the *LS*-coupling scheme is valid and the spin moment operator **S** is well defined, which is true for $3d$- and $4f$-element compounds, but not for the $5f$ electrons of actinides. For the latter materials the *LS* coupling scheme is not valid, but the *jj* coupling or intermediate coupling schemes.

That means that the widely used[38,41] form of the spin-polarized potential based on the LSDA cannot be applied for actinides, because the LSDA neglects terms in both spin density and potential that are off diagonal in spin variables. Those terms appear due to spin-orbit coupling [Eq. (8)] and suppress spin moment formation while the exchange (Hund) part of the Coulomb interaction prefers a fully spin-polarized state with occupation and potential matrices diagonal in spin variables. Competition between the spin-orbit coupling and exchange interaction determines the magnetic state of the $5f$ shell. Neglecting potential terms that are off diagonal in spin variables in the methods using the LSDA potential enhances the tendency to spin moment formation. (In Sec. III we show that neglecting potential terms off diagonal in spin variables in the LDA+U+SO method results in a very strong increase of the calculated spin and orbital moment values.) This fact could explain why an antiferromagnetic ground state with a large value of the spin moment was obtained in fully relativistic spin-polarized method calculations,[38,41] in disagreement with experimental data.[2,4,21]

III. METALLIC PLUTONIUM

A. δ phase of plutonium

Phase diagram of plutonium is the most complex of all elements.[71] Of special interest is the fcc δ phase of Pu (a =4.636 Å). A phase transition from the δ phase to the low-temperature monoclinic α-plutonium phase (a=6.183 Å, b =4.824 Å, c=10.973 Å, and β=101.79°) is accompanied with a very large (19%) volume contraction.

In the LDA+U calculation scheme the values of direct (U) and exchange (J_H) Coulomb parameters should be determined as the first step of the calculation procedure. It can be done in an *ab initio* way via constrained LDA calculations.[63,64] In our calculations the Hund exchange parameter J_H was found to be J_H=0.48 eV, much smaller than the value used in previous LDA+U studies.[32] The obtained Coulomb repulsion parameter value U=3.84 eV is in good agreement with the previously used U=4 eV.[20,30,59,72–74] The Coulomb interaction parameters describe a *screened* Coulomb interaction between $5f$ electrons and hence crucially depend on the channels of screening taken into account in the constrained LDA calculations. That is true for the direct Coulomb parameter U, but the exchange Coulomb parameter J_H corresponds to the *difference* of the interaction energy for the electron pairs with the opposite and the same spin directions. As the screening process is defined by the charge but not the spin state of the ion, the screening contribution is canceled for the exchange Coulomb interaction and the parameter J_H does not depend on the screening channel choice. For example, for $3d$-element compounds, the direct Coulomb interaction parameter varies from 8 eV for late transition metal oxides (NiO and CuO) to 3 eV for the beginning of the row (Ti and V oxides). At the same time the exchange Coulomb parameter J_H is in the range 0.85–0.95 eV for the whole $3d$ row. In our constrained LDA calculations we have found that J_H is equal to 0.48 eV within the accuracy 0.01 eV for both metallic Pu phases and for all plutonium compounds investigated in the present work. Physically, a much smaller value of the Hund parameter J_H for Pu $5f$

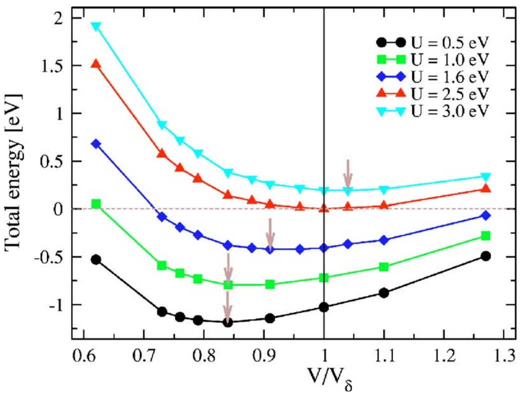

FIG. 2. (Color online) Total energy as a function of volume for fcc Pu calculated with various values of Coulomb parameter U (V_δ corresponds to the experimental volume value for Pu in the δ phase). Arrows indicate minima of the curves giving equilibrium volume values. The calculated equilibrium volume is equal to the experimental value for the curve with U=2.5 eV.

compared with the corresponding values for 3d, 4d, and 4f orbitals, where J_H is in the range 0.7–1 eV, can be understood by taking into account the more extended spatial range of the 5f orbitals, compared to the above-mentioned orbitals.

In our constrained LDA calculations it was supposed that the f shell is screened by s, p, and d electrons, so that the 5f electrons were considered to be completely localized and did not participate in the screening. The LDA calculations with spin-orbit coupling taken into account show [Fig. 1(a)] well-separated subbands corresponding to the total moment values j=5/2 and 7/2 with the Fermi level crossing the top of the j=5/2 band. This splitting of the 5f shell into almost filled $f^{5/2}$ and empty $f^{7/2}$ subshells can justify an additional screening of $f^{5/2}$ electrons by $f^{7/2}$ ones. In the constrained LDA calculations with this screening channel taken into account, the Coulomb parameter value was obtained as U=0.44 eV.

Plutonium is considered to be on the edge between the completely localized 5f electrons of americium and their itinerant nature for early actinides, so that neither limit, completely localized or totally itinerant, is appropriate for Pu 5f electrons. The correct value of U should be somewhere in between the values calculated in those two limits (3.84 eV without any f electrons participating in the screening and 0.44 eV for full $f^{7/2}$ screening). As an additional requirement to determine the U value we have chosen equality of the calculated equilibrium volume of fcc Pu to the experimental value of the δ phase (see Fig. 2). This requirement is satisfied for U=2.5 eV and we used this Coulomb interaction parameter value in the LDA+U+SO calculations for metallic Pu in both α and δ phases and for all Pu compounds investigated in this work.

The LDA+U+SO calculations for metallic Pu in the δ phase gave a nonmagnetic ground state with zero values of spin **S**, orbital **L**, and total **J** moments. The occupation matrix Eq. (2) has six eigenvalues close to unity (see in Table I the row corresponding to J_H=0.48 eV) and is nearly diagonal in the $\{jm_j\}$ basis of eigenfunctions of total moment **J**. That gives an f^6 configuration of the Pu ion in the jj coupling scheme. In Fig. 1(b) the partial densities of states for $f^{5/2}$ and $f^{7/2}$ subshell orbitals are presented. In agreement with the occupation matrix analysis one can see an almost completely filled $f^{5/2}$ band with the Fermi level at the top of it, and an empty $f^{7/2}$ band. The separation between the centers of these bands is ≈4 eV.

The origin of this nonmagnetic LDA+U+SO solution can be traced to the results of standard LDA calculations without Coulomb correlation correction but with spin-orbit coupling taken into account [see Fig. 1(a)]. The 5f band is split by spin-orbit coupling into well-pronounced $f^{5/2}$ and $f^{7/2}$ bands with a separation between their centers ≈1.5 eV. The Fermi level is in the pseudogap between subbands, closer to the top of the $f^{5/2}$ band. Comparing Figs. 1(a) and 1(b) one can see that taking into account Coulomb correlations via the LDA +U correction potential Eq. (6) does not change the band structure qualitatively. The only effect is that the separation between subbands increases from 1.5 to 4 eV, which corresponds to the value of U=2.5 eV. Another effect of Coulomb interaction is the almost pure orbital character of $f^{5/2}$ and $f^{7/2}$ bands in the LDA+U+SO calculations compared with a significant admixture of $f^{5/2}$ orbitals to the nominally $f^{7/2}$ band and vice versa in the LDA results [Fig. 1(a)]. One can say that the nonmagnetic J=0 solution with the $f^{5/2}$ subshell filled with six electrons and an empty $f^{7/2}$ band is already

TABLE I. Electronic configuration of Pu ion 5f shell in δ-plutonium calculated with the LDA+U+SO method (U=2.5 eV) for various values of the Hund exchange parameter J_H. The largest values of the occupation matrix off-diagonal elements (OD) in $\{LS\}$ and $\{jm_j\}$ basis sets are given in the second and the third columns. The seven largest eigenvalues of the occupation matrix are presented from the fourth to the tenth columns. Columns from eleven to thirteen show the calculated values for spin (S), orbital (L), and total (J) moments (Ref. 75). The last four columns contain partial contributions of f^5 and f^6 configurations and types of coupling for the 5f shell of plutonium ion (see the text for explanations).

J_H (eV)	OD$_{\{LS\}}$	OD$_{\{jm_j\}}$	Largest eigenvalues	S	L	J	f^5	f^6	jj	LS
0.40	0.431	0.022	0.041 0.885 0.885 0.910 0.910 0.910 0.910	0	0	0	0	1.00	1.00	0.00
0.43	0.432	0.021	0.041 0.886 0.886 0.911 0.911 0.911 0.911	0	0	0	0	1.00	1.00	0.00
0.48	0.433	0.008	0.040 0.889 0.889 0.912 0.912 0.912 0.912	0	0	0	0	1.00	1.00	0.00
0.49	0.435	0.019	0.040 0.889 0.890 0.912 0.912 0.913 0.914	0.083	0.099	0.016	0.01	0.99	0.97	0.03
0.50	0.433	0.127	0.041 0.880 0.884 0.909 0.918 0.918 0.925	0.582	0.692	0.110	0.04	0.96	0.81	0.19
0.55	0.412	0.279	0.045 0.838 0.884 0.912 0.929 0.938 0.945	1.369	1.640	0.271	0.11	0.89	0.54	0.46
0.60	0.392	0.346	0.050 0.823 0.888 0.916 0.935 0.949 0.956	1.746	2.064	0.318	0.13	0.87	0.41	0.59

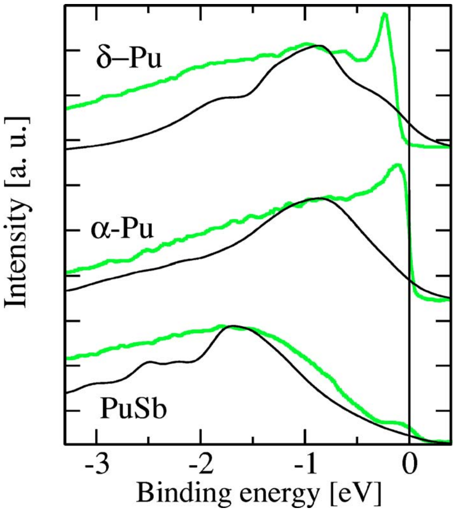

FIG. 3. (Color online) Experimental [PES spectra for δ- and α-plutonium with $h\nu$=41 eV and T=80 K (Ref. 10) and angle-integrated PES for PuSb at 15 K (Ref. 126)] and calculated (thin line) photoemission spectra for metallic Pu in δ and α phases and for PuSb.

"preformed" in the LDA. The role of Coulomb correlations in the LDA+U method is to make it more pronounced with a pure orbital nature of the bands and increased energy separation between them. Usually, applying the LDA+U correction to the LDA method leads to orbital polarization and hence to nonzero values of spin and orbital moments, in contrast to our S=0, L=0, and J=0. In our case even the LDA solution shows the f shell almost polarized into six fully occupied j=5/2 orbitals and eight almost empty j=7/2 orbitals, and the LDA+U potential does not change the already existing orbital polarization.

Photoemission spectroscopy is the direct tool for investigation of electronic structure. The total densities of states obtained in our LDA+U+SO study were multiplied by the Fermi function corresponding to the temperature of experiment and broadened with a 0.2 eV Lorentian to account for the instrumental resolution (see Fig. 3). With the exception of the sharp peak near the Fermi level the overall agreement between experimental and calculated spectra for δ-Pu is satisfactory. This peak is usually considered as a sign of strong many-body effects, which can be described by the DMFT (see Refs. 59 and 58) but not by the static mean-field approximation which is the basis of the LDA+U method. However, the LDA+U can reproduce the lower and upper Hubbard bands, into which the partially filled f band is split by Coulomb interaction. Indeed, the peak at ≈1 eV in the experimental spectrum corresponding to the lower Hubbard band is well described by the calculated spectrum.

Our results are in agreement with the experimental data showing the absence of ordered or disordered magnetic moments for plutonium in both δ and α phases.[2,4,21] However, all previous electronic structure calculations gave a magnetic (usually antiferromagnetic) state lower in energy than the nonmagnetic one. To clarify this problem we have carried out an investigation of the stability of our nonmagnetic ground state toward the parameters of the calculations. The influence of the different approximations for the exchange interaction term in the Hamiltonian was investigated as well.

As the first step we varied the value of the exchange Coulomb parameter J_H around the J_H=0.48 eV value obtained in our constrained LDA calculations. In Table I the results of the LDA+U+SO calculations with J_H values in the range from 0.40 to 0.60 eV are presented. One can see that even a 15% increase of the J_H value is enough to result in a magnetic ground state with sizable values of spin and orbital moments. However, the total moment value remains very small, less than 0.3μ_B.

In addition to the moment values, in Table I we show values of the largest off-diagonal elements of the occupation matrix Eq. (2) in $\{LS\}$ and $\{jm_j\}$ bases. As one can see, for J_H=0.48 eV obtained in the constrained LDA calculations, the $\{jm_j\}$ basis is the most appropriate with the largest off-diagonal elements values less than 0.01, while in the $\{LS\}$ basis these values are very large (more than 0.4). That can be interpreted as a pure case of jj coupling with a well-defined total moment ($\mathbf{J}$) but not spin ($\mathbf{S}$) and orbital ($\mathbf{L}$) moments. With increase of the J_H value the off-diagonal elements in the $\{jm_j\}$ basis grow rapidly and for J_H=0.60 eV become comparable with the off-diagonal elements in the $\{LS\}$ basis, making the jj coupling scheme not valid any more. As the off-diagonal elements in the $\{LS\}$ basis are still very large (≈0.4), the LS coupling scheme is also not appropriate and an intermediate coupling scheme is needed to describe the magnetic solution.

The eigenvalues of the occupation matrix Eq. (2) presented in Table I show six orbitals with occupancies close to unity for all values of J_H. Considering that, one can conclude that the Pu ion is predominantly in the f^6 configuration in the magnetic as well as in the nonmagnetic state. Only nonmagnetic ground states corresponding to values of the Hund parameter $J_H \leqslant 0.48$ eV can be interpreted as a pure f^6 configuration in the jj coupling scheme. Magnetic solutions for $J_H > 0.48$ eV correspond to a predominantly f^6 configuration in an intermediate coupling scheme.

In order to estimate how close a calculated state is to one of the pure states (f^6 or f^5 configurations, in the jj or LS coupling schemes) we propose the following simple formula using calculated values of spin (S), orbital (L), and total (J) moments. The total moment value is the same in both coupling schemes (jj or LS): J=0 for f^6 and J=5/2 for f^5. If we have a mixed state $(1-x)f^6+xf^5$ then x can be defined as $x=J/2.5$. The spin S and orbital L moment values for the f^6 configuration are equal to zero in the jj coupling scheme and S=3, L=3 in the LS coupling scheme. For the f^5 configuration they are $S=5/14\approx 0.36$, $L=20/7\approx 2.86$ in the jj coupling scheme and S=5/2, L=5 in the LS coupling scheme. One can define a mixed coupling scheme with a contribution of jj coupling equal to y and of LS coupling corresponding to $(1-y)$. In this scheme the calculated values of orbital and spin moments will be

$$L = x[2.86y + 5(1-y)] + (1-x)[0y + 3(1-y)], \quad (11)$$

$$S = x[0.36y + 2.5(1-y)] + (1-x)[0y + 3(1-y)]. \quad (12)$$

These formulas allow us to determine the coefficient y.

TABLE II. Electronic configuration of Pu ion in δ-plutonium calculated with the LDA+U+SO method as a function of the $5f$ band shift value Δ. (Notations are the same as for Table I.)

Δ (eV)	$\mathrm{OD}_{\{LS\}}$	$\mathrm{OD}_{\{jm_j\}}$	Largest eigenvalues	S	L	J	f^5	f^6	jj	LS
0	0.433	0.008	0.040 0.889 0.889 0.912 0.912 0.912 0.912	0	0	0	0	1.00	1.00	0.00
0.14	0.431	0.012	0.040 0.879 0.879 0.906 0.906 0.906 0.906	0.023	0.029	0.006	0	1.00	0.99	0.01
0.27	0.431	0.044	0.040 0.864 0.866 0.897 0.900 0.903 0.905	0.210	0.286	0.076	0.03	0.97	0.93	0.07
0.41	0.427	0.188	0.042 0.642 0.865 0.919 0.919 0.934 0.942	0.920	1.700	0.780	0.31	0.79	0.70	0.30
0.82	0.432	0.256	0.043 0.254 0.910 0.924 0.942 0.954 0.959	1.316	3.040	1.724	0.69	0.31	0.56	0.44
1.36	0.419	0.256	0.040 0.086 0.886 0.886 0.938 0.947 0.962	1.378	3.609	2.231	0.89	0.11	0.53	0.47

The values of the coefficients x and y calculated in this way are shown in Table I. For values of the Hund parameter $J_H \leqslant 0.48$ eV they correspond to the pure f^6 configuration in a 100% jj coupling scheme. With increase of the J_H value the contribution of LS coupling increases, and for J_H close to 0.60 eV both coupling schemes gave approximately equal contributions, demonstrating a clear sample of an intermediate coupling scheme. However, the configuration is still predominantly f^6 with not more than 10% admixture of f^5.

Not only the strength of the exchange interaction parameter J_H is crucial for the magnetism of the $5f$ shell in metallic Pu. The Fermi level is at the top of the $f^{5/2}$ band [see Fig. 1(a)] and a small shift of the relative energy position of the $5f$ and other states might lead to redistribution of electrons between $5f$ and spd bands and hence change the f configuration and magnetic state of the Pu ion. To investigate this effect we ran the LDA+U+SO calculations with a constant positive potential Δ acting on the $5f$ electrons, which should result in a charge flow from $5f$ bands to spd bands (see Table II). Even a relatively small value of the shift ($\Delta=0.41$ eV) is enough to produce a well-pronounced magnetic ground state with a sizable admixture of f^5 configuration (about one-third). For a shift value equal to 1.36 eV the Pu ion is in a pure f^5 configuration with very large values of spin, orbital, and total moments.

These constrained LDA+U+SO calculations demonstrate that the relative position of the $5f$ and other bands is of great importance for the resulting configuration and magnetic state of the Pu ion. Later we will show that in all plutonium compounds investigated in this work we obtained a magnetic ground state in contrast to the nonmagnetic one for metallic Pu.

In order to study the influence of the different approximations for the exchange interaction term in the Hamiltonian first we performed the LSDA+U (the electron density and LDA potential were used in spin-polarized forms) calculations with the same Coulomb interaction parameter values as in Ref. 30 [the exchange parameter value corresponds to $J_H=0.85$ eV (Ref. 32) and $U=4$ eV]. In this calculation a strong magnetic state with a configuration close to f^5 was obtained in agreement with the results of Ref. 30. The $5f$ band dispersion is presented in Fig. 4(a) (the width of the band curve is proportional to the contribution of $5f$ states to the band). It agrees well with the corresponding figure in Ref. 30. Decreasing the Coulomb exchange parameter value J_H from 0.85 to 0.48 eV (obtained in our constrained LDA calculation) gave a magnetic solution with spin $S=2.5$ but the $5f$ configuration is now closer to f^6 than to f^5 (the Fermi level [Fig. 4(b)] is now above the top of the band which was cut by the Fermi level in Fig. 4(a)). As the next step we used the LDA+U+SO calculation scheme Eqs. (1)–(8) with a non-spin-polarized electron density and the LDA potential but keeping the Hund parameter $J_H=0.85$ eV (Refs. 30 and 32) [see Fig. 4(c)]. In this calculation we found a magnetic ground state ($S=2.5$, $L=2.7$, and $J=0.2$) with a configuration close to f^6. Only the calculation by the LDA+U+SO method with the Coulomb exchange parameter value obtained in the constrained LDA calculations ($J_H=0.48$ eV) gave [see Fig. 4(d)] a nonmagnetic state with $S=0$, $L=0$, and $J=0$.

In Sec. II we noted that the use of a spin-polarized potential based on the LSDA is equivalent to neglecting exchange potential terms off diagonal in the spin variables and hence increases the tendency to spin moment formation. To check this we have performed the LDA+U+SO calculations with the terms off diagonal in the spin variables in the LDA+U potential [Eq. (6)] set to zero ($U=2.5$ eV and $J_H=0.48$ eV). As a result we indeed obtained a magnetic ground state (see Table III) which is close to the results of the LSDA+U calculations.[33,59] To compare with the results of the fully relativistic spin-polarized calculation we performed the LDA+U+SO calculations with the terms off diagonal in spin the variables in the LDA+U potential [Eq. (6)] set to zero using the value of the Coulomb parameter $U=J_H=0.48$ eV. In Ref. 76 it was shown that $U-J_H$ can be regarded as an effective Coulomb interaction parameter U_{eff} in the LSDA+U calculations, so the choice of $U=J_H$ is equivalent to $U_{eff}=0$. Such calculations gave a solution with large

TABLE III. Calculated values for spin, orbital, and total moments from the LDA+U+SO calculations with the elements off diagonal in the spin variables in the potential matrix Eq. (6) set to zero. For comparison the results of the LSDA and LSDA+U calculations are presented (Ref. 75).

Method	S	L	J
LDA+U+SO ($U=2.5$ eV, $J_H=0.48$ eV)	2.43	3.57	1.14
LSDA+U (Ref. 33)	2.50	3.70	1.20
LSDA+U (Ref. 59)	2.55	3.90	1.45
LDA+U+SO ($U=J_H=0.48$ eV)	1.70	2.30	0.60
LSDA (Ref. 41)	2.04	1.75	0.29
LSDA (Ref. 33)	2.11	1.94	0.17
LSDA (Ref. 38)	2.25	2.40	0.15

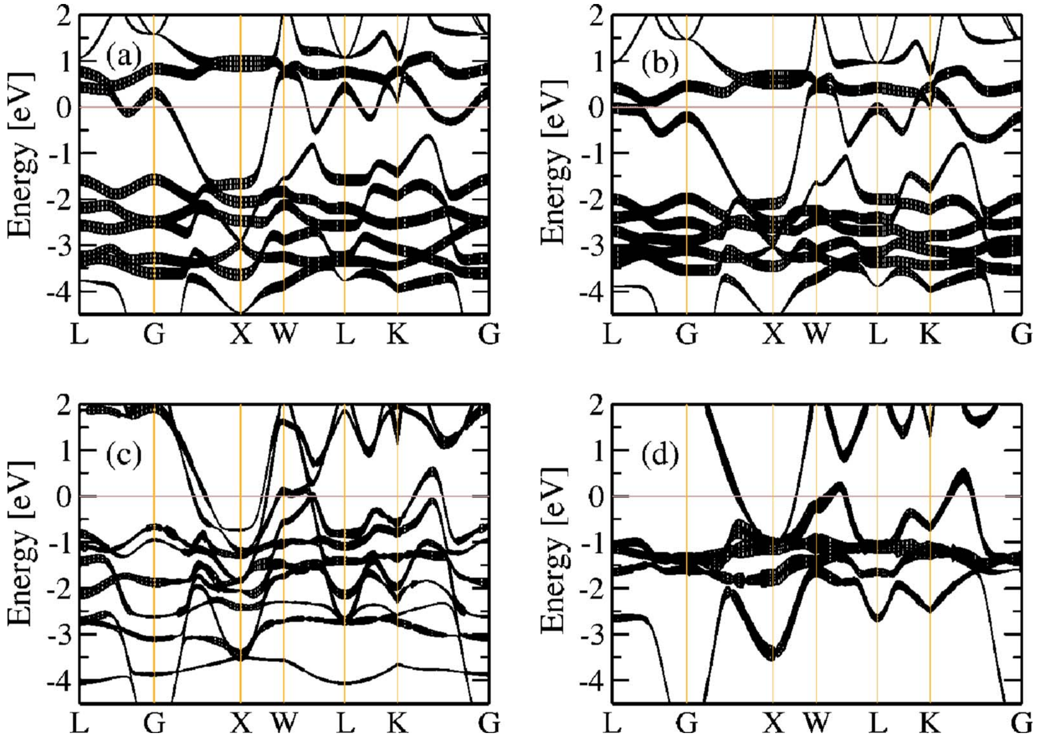

FIG. 4. (Color online) (a) Band structure of δ-Pu (the width of the line shows the contribution of the 5f states to the particular band) from the LSDA+U calculations with Coulomb parameter values U=4 eV and J_H=0.85 eV. (b) The same as (a) but for J_H=0.48 eV. (c) The same as (a) but by the LDA+U+SO method (U=4 eV and J_H=0.85 eV). (d) Same as (c) but for J_H=0.48 eV (see text).

values of spin and orbital moments (see Table III) similar to the LSDA results.

B. α phase of plutonium

A transition from the δ to the α phase can be described as a volume contraction by 19% and a monoclinic distortion of the fcc lattice. We performed the LDA+U+SO calculation for the fcc lattice with the volume per Pu atom corresponding to the α phase. That allowed us to separate the influences on the electronic structure and magnetic properties of the volume contraction and lattice distortion. The result is the same nonmagnetic solution, S=0, L=0, and J=0 in the f^6 configuration, as was obtained for the δ phase. Variation of the Hund parameter J_H has shown that for Pu in the fcc structure with the volume of the α phase the nonmagnetic solution is a little more stable than for the δ-phase volume (while in the latter case even a 15% increase of J_H was enough to produce a magnetic state, for the α-phase volume a 20% increase is needed).

The LDA+U+SO calculation for the real monoclinic crystal structure of the α phase (see Fig. 5) also gave a nonmagnetic ground state with S=0, L=0, and J=0 in the f^6 configuration. Compared with the results for the δ phase (Fig. 1) one can see that the bands become broader [Fig. 5(a)] due to the smaller volume and hence increased hybrid-

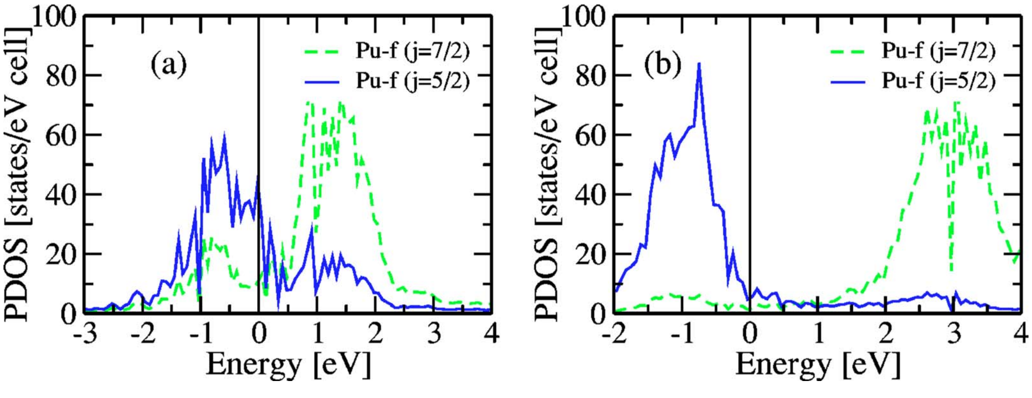

FIG. 5. (Color online) Partial $f^{5/2}$ and $f^{7/2}$ contributions to 5f band densities of states of monoclinic α-plutonium calculated with the LDA (a) and LDA+U+SO method (b).

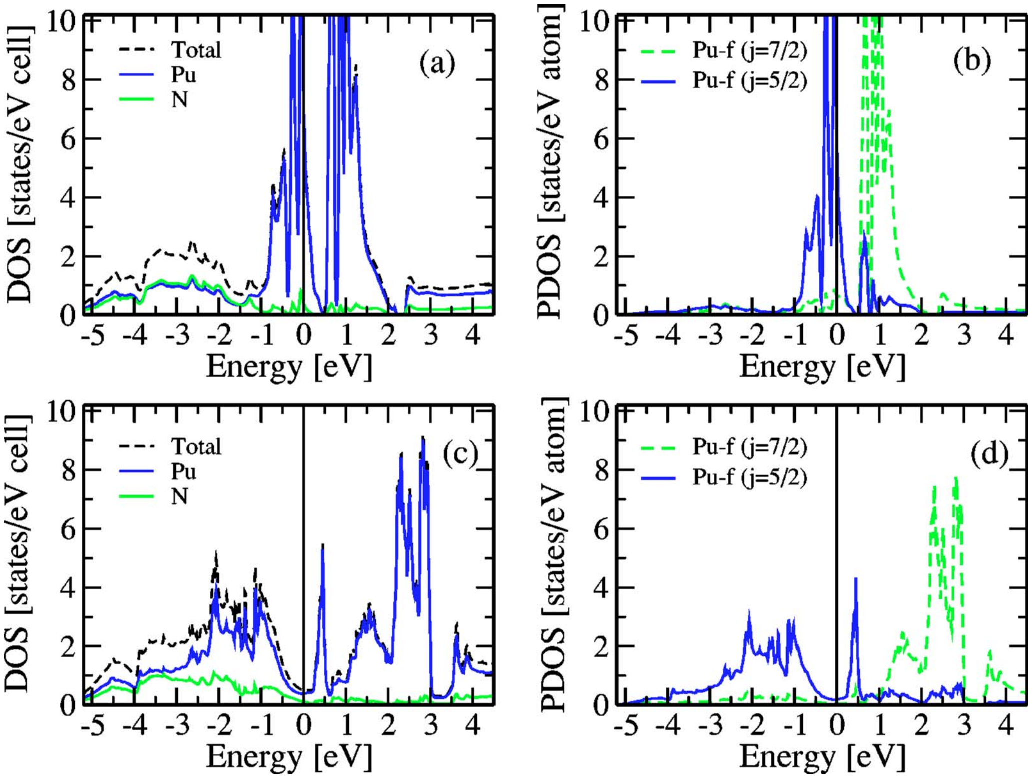

FIG. 6. (Color online) (a) Total and partial densities of states of PuN calculated in the LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuN from the LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

ization strength. Consequently the $f^{5/2}$ and $f^{7/2}$ bands have much more mixed character compared with the δ-phase bands [Fig. 1(a)]. However, after taking into account Coulomb interaction in the LDA+U+SO calculations [Fig. 5(b)] the band structure becomes very similar to the case of the δ phase [Fig. 1(b)]. The $f^{5/2}$ and $f^{7/2}$ bands have now pure orbital character. The $f^{5/2}$ band is almost completely filled with the Fermi level at the top of it, and the $f^{7/2}$ band is empty. The separation between the centers of the bands is ≈ 4 eV.

The calculated photoemission spectrum (see Fig. 3) is not very different from the corresponding curve for the δ phase except that it is smoother and does not show higher- and lower-energy shoulders. The sharp peak near the Fermi level, which is stronger in the experimental spectrum for the α-phase than for the δ-phase spectrum, is missing as in the δ phase. Again, we expect that DMFT can solve this problem.[53–55] But the peak in the experimental spectrum at ≈ 1 eV corresponding to the lower Hubbard band is well described by the calculated spectrum.

As we have shown above, the calculation scheme presented here is different from those used in previous investigations of plutonium electronic structure and magnetic properties. A resulting nonmagnetic ground state (Pu ion in the f^6 configuration with the jj coupling scheme) was not obtained in the other calculations. In order to check the validity of our method we performed calculations for a series of Pu compounds. The main aim of these calculations was to investigate the magnetic properties for these compounds and to compare the results with the available experimental data.

IV. PLUTONIUM COMPOUNDS

A. PuN

Plutonium mononitride crystallizes in a rock salt-type structure with $a=4.905$ Å.[77] Neutron diffraction showed no long-range order or magnetic moments larger than $0.25\mu_B$.[78] From the magnetic susceptibility and specific heat measurements an antiferromagnetic transition at $T_N=13$ K was proposed.[79] According to another magnetic susceptibility curve, PuN is a Curie-Weiss paramagnet with $\mu_{eff}=1.08\mu_B$.[80] The electronic structure of PuN was calculated in the L(S)DA with and without relativistic correction.[81] The SIC LSDA method showed that valency +5 is energetically preferred in the model with partially localized $5f$ electrons of the Pu ion.[49]

Figures 6(a) and 6(b) show the total and partial f densities of states of PuN obtained in our LDA with spin-orbit coupling calculation (when the Coulomb interaction correction was switched off). The nitrogen $2p$ states are strongly hybridized with the Pu f states and the Fermi level is located inside the $j=5/2$ subband. While the $j=5/2$ and $7/2$ subbands are well separated from each other [see Fig. 6(b)], they do not have pure orbital character, with a strong admixture of $j=5/2$ states to the formally $j=7/2$ subband. The results of the LDA+U+SO calculation are presented in Figs. 6(c) and 6(d). In contrast to the metallic Pu case the Coulomb inter-

TABLE IV. Electronic configuration of Pu ion in various plutonium compounds calculated with the LDA+U+SO method. (Notations are the same as for Table I).

Compound	$\mathrm{OD}_{\{LS\}}$	$\mathrm{OD}_{\{jm_j\}}$	Largest eigenvalues	S	L	J	f^5	f^6	jj	LS
PuN	0.436	0.239	0.118 0.162 0.923 0.930 0.960 0.965 0.978	1.279	3.339	2.060	0.82	0.18	0.57	0.43
$\mathrm{PuCoGa_5}$	0.426	0.226	0.029 0.796 0.883 0.897 0.922 0.939 0.941	1.144	1.594	0.450	0.18	0.82	0.62	0.38
$\mathrm{PuRh_2}$	0.348	0.302	0.127 0.525 0.610 0.883 0.908 0.924 0.927	1.546	3.421	1.875	0.75	0.25	0.46	0.54
$\mathrm{PuSi_2}$	0.441	0.142	0.070 0.907 0.916 0.939 0.949 0.960 0.962	0.692	0.829	0.137	0.05	0.95	0.77	0.23
PuTe	0.441	0.253	0.026 0.895 0.904 0.908 0.928 0.940 0.946	0.907	1.069	0.162	0.06	0.94	0.70	0.30
PuSb	0.453	0.320	0.046 0.127 0.959 0.961 0.973 0.981 0.982	1.583	3.650	2.067	0.83	0.17	0.44	0.56

action correction has not only increased the energy separation between $j=5/2$ and $7/2$ subbands, but also led to the splitting of the $j=5/2$ subband into occupied and empty states [see the peak of $j=5/2$ character just above the Fermi energy on Fig. 6(d)]. As this split-off band contains one electron per Pu ion, one can conclude that our results correspond to the configuration f^5 in agreement with the formal Pu valency +3 in PuN.

In Table IV (the first row corresponds to PuN) the calculated values for spin, orbital, and total moments are presented. The total moment $J=2.218$ is close to the ideal value $j=5/2$ for the f^5 configuration. The five largest eigenvalues of the occupation matrix also show a well-defined f^5 configuration. The analysis of the occupation matrix off-diagonal elements shows that in the $\{jm_j\}$ basis the values of those elements are nearly two times smaller than the corresponding values for the $\{LS\}$ basis. That corresponds to the intermediate coupling scheme closer to jj coupling. The analysis based on the calculated values for spin, orbital, and total moments [see Eq. (12) in Sec. III A] gave 89% of f^5 and 11% of f^6 configuration with 57% of jj and 43% of LS coupling.

In order to compare our results with the experimental magnetic measurement data we should obtain the magnetic moment value using calculated values of spin (S), orbital (L), and total moments (J). In the cases when spin-orbit coupling is weak and the Russell-Saunders coupling (LS coupling) scheme is valid the total magnetic moment value can be calculated as

$$M_{tot}=2S+L. \tag{13}$$

However, for strong spin-orbit coupling when the jj or intermediate coupling scheme should be used, this problem becomes much more complicated. There is no general solution of this problem for the intermediate coupling scheme, and for jj coupling it can be solved only for free ions in pure configuration. An effective paramagnetic moment obtained from susceptibility measurements using the Curie-Weiss law can be calculated as

$$\mu_{eff}=g\sqrt{J(J+1)}\mu_B. \tag{14}$$

The problem is to define the Landé g factor which can be calculated for pure f^5 and f^6 configurations in the LS or jj coupling scheme. As for the f^6 configuration total moment $J=0$, one needs to calculate the g factor for the f^5 configuration only. For the ground state of the f^5 configuration in the jj coupling scheme the Landé factor is $g_{jj}=6/7\approx 0.86$. In the LS coupling scheme its value is $g_{LS}=2/7\approx 0.29$. As the latter value is nearly three times larger than the former, g_{jj} and g_{LS} can give only upper and lower limits of the g factor for the case of intermediate coupling.

In Table V the values of effective paramagnetic moments calculated using Eq. (14) are presented. In addition to μ_{eff}^{LS} and μ_{eff}^{jj} calculated using Landé factors g_{LS} and g_{jj}, respectively, we have calculated their weighted value μ_{eff}^{calc} using the relative weights of LS and jj coupling obtained from Eq. (12).

The results for PuN (the first row of Table V) gave $\mu_{eff}^{calc}=1.54\mu_B$, in reasonable agreement with the experimental value $\mu_{eff}^{expt}=1.08\mu_B$.

B. $\mathrm{PuCoGa_5}$

Since first reported in 2002 by Sarrao *et al.*,[82] the superconductor $\mathrm{PuCoGa_5}$ has attracted special attention, being the first Pu-containing superconductor in the well-known super-

TABLE V. Values of effective paramagnetic moments (in Bohr magnetons μ_B) calculated from the total moment value J in jj and LS coupling schemes μ_{eff}^{LS} and μ_{eff}^{jj} and their weighted value μ_{eff}^{calc} in comparison with experimental data μ_{eff}^{expt} (see text).

Compound	J	jj	LS	μ_{eff}^{jj}	μ_{eff}^{LS}	μ_{eff}^{calc}	μ_{eff}^{expt}	Ref.
PuN	2.060	0.57	0.43	2.16	0.72	1.54	1.08	80
$\mathrm{PuCoGa_5}$	0.450	0.62	0.38	0.69	0.23	0.52	0.68	82
$\mathrm{PuRh_2}$	1.875	0.46	0.54	1.99	0.66	1.27	0.88	99
$\mathrm{PuSi_2}$	0.137	0.77	0.23	0.34	0.11	0.23	0.54	101 and 103
PuTe	0.162	0.70	0.30	0.37	0.12	0.30		
PuSb	2.067	0.44	0.56	2.16	0.72	1.35	1.00	122

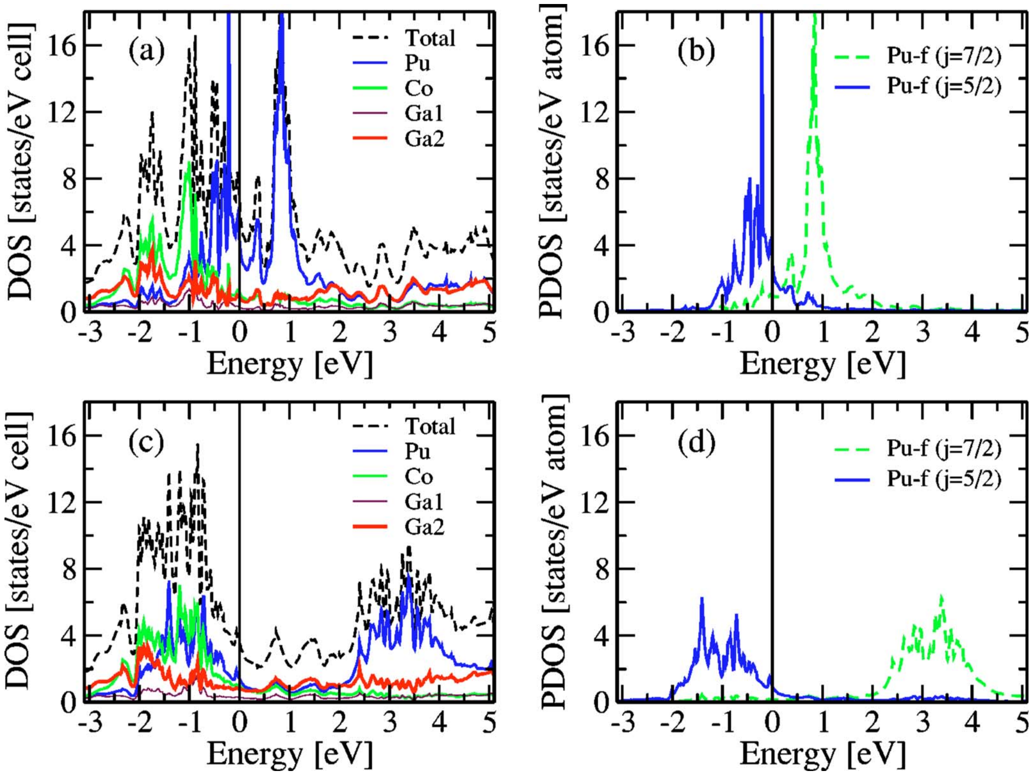

FIG. 7. (Color online) (a) Total and partial densities of states of PuCoGa$_5$ calculated in the LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu 5f band for PuCoGa$_5$ from the LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

conductor class of "115" materials.[83–85] Its superconducting (SC) temperature T_c=18.5 K is an order of magnitude higher than for other 115 superconductors.[84,85] The specific heat coefficient value γ=77 mJ mol^{-1} K^{-2} and Curie-Weiss behavior of the magnetic susceptibility with μ_{eff}=0.68μ_B are indicative of unconventional superconductivity in PuCoGa$_5$.[82,86–90] Tanaka *et al.*[91] used the periodic Anderson model to describe the d-wave superconducting state of PuCoGa$_5$. Its isostructural counterpart PuRhGa$_5$ shows analogous properties but with a lower value of the SC transition temperature T_c=8 K.[92]

PuCoGa$_5$ crystallizes in the tetragonal $P4/mmm$ space group with a=4.232 Å and c=6.782 Å.[82] An electronic structure calculation of PuCoGa$_5$ was performed in the fully relativistic full-potential method of local orbitals.[93] In that work the paramagnetic state has a total energy value substantially higher than the ferromagnetic and antiferromagnetic (AFM) solutions.

The LDA calculation without spin-orbit coupling[83,94] showed the Fermi level crossing the Pu 5f band manifold without any splitting. Another calculation by the relativistic LAPW method[95] gave a Fermi surface analogous to that of the CeMIn$_5$ series. The microscopic model for compounds with f ions in the jj-coupled state was extended to PuCoGa$_5$ in Ref. 96. Antiferromagnetic order was proposed in the electronic structure calculation in Refs. 97 and 98.

In PuN 5f bands are only present at the Fermi level while the fully occupied N p band is situated substantially lower [Fig. 6(a)]. In contrast to that, in PuCoGa$_5$ the Co d and Ga p bands cross the Fermi level in addition to the 5f bands of Pu [see Fig. 7(a)] so that the 5f states contribute only one-third to the density of states value at the Fermi energy. This fact leads to a very complicated general band structure for this compound [Fig. 6(a)] but the partial 5f density of states presented on Fig. 6(b) shows well-pronounced $f^{5/2}$ and $f^{7/2}$ subbands with ≈1.5 eV separation between them. This picture is very close to the results for the δ phase of metallic Pu [Fig. 1(b)] but with a larger overlapping of $f^{5/2}$ and $f^{7/2}$ subbands and the position of the Fermi level a little deeper inside the $f^{5/2}$ band. This is the effect of a stronger hybridization of 5f orbitals with Co d and Ga p states in PuCoGa$_5$ compared with metallic Pu.

Due to the Coulomb interaction correction in the LDA +U+SO calculations [Figs. 6(c) and 6(d)] the separation between the $f^{5/2}$ and $f^{7/2}$ subbands is up to 4 eV; the orbital character of the bands becomes almost pure as in metallic Pu [Fig. 1(d)]. In Table IV (the second row corresponds to PuCoGa$_5$) the calculated values for spin, orbital, and total moments are presented. The Pu ion for our solution is predominantly in the f^6 configuration but with a significant (18%) admixture of f^5 configuration. Sizable values of spin and orbital moments together with a relatively small value of the total moment gave an intermediate coupling scheme closer to jj coupling; as in PuN.

We would like to note that, in spite of a band structure for 5f states very similar to that of metallic Pu [compare Figs. 7(b) and 1(b)] in the LDA calculations, the LDA+U+SO calculations scheme gave a magnetic ground state for PuCoGa$_5$ in agreement with experimental data.[82,86–89] In Table V (second row) the values of the effective paramag-

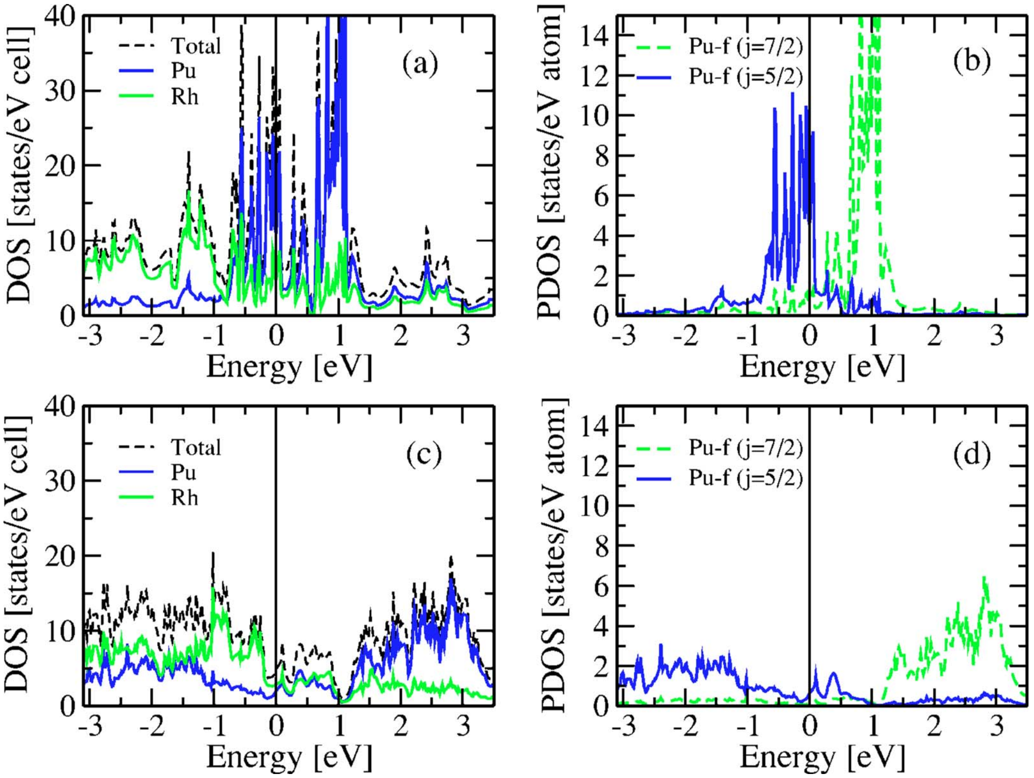

FIG. 8. (Color online) (a) Total and partial densities of states of PuRh_2 calculated in the LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuRh_2 from the LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

netic moments calculated using Eq. (14) are presented. The weighted value $\mu_{eff}^{calc}=0.52\mu_B$ is smaller than the experimental $\mu_{eff}^{expt}=0.68\mu_B$, which is very close to the $\mu_{eff}^{jj}=0.69\mu_B$ calculated with the Landé g factor g_{jj} obtained in the jj coupling scheme.

C. PuRh_2

PuRh_2 crystallizes in the Laves structure (C_{15}) $a=7.488$ Å.[99] From the magnetic susceptibility[99] PuRh_2 is a Curie-Weiss paramagnet with $p_{eff}=0.88\mu_B$, $\Theta_p=-49$ K, and $\chi_{max}=4.4\times10^{-3}$ emu mol^{-1}. According to the specific heat results with $\gamma=145$ mJ mol^{-1} K^{-2} and $\theta_D=190$ K, PuRh_2 was classified as a "middle-weight" fermion system without temperature dependence of γ in the region of low temperatures.[100]

The dominant contribution to the PuRh_2 band structure gives a broad partially filled Rh d band [Fig. 8(a)]. Pu $5f$ states [Fig. 8(b)] show significant hybridization with the Rh d band. However, the general feature common to metallic Pu and all Pu compounds investigated in this work, the separation into $f^{5/2}$ and $f^{7/2}$ subbands, can still be seen here [Fig. 8(b)]. The position of the Fermi level inside the $f^{5/2}$ band, as in the PuN case [Fig. 6(b)], shows that the resulting configuration should be close to f^5. Indeed, the LDA+U+SO calculations gave [Figs. 8(c) and 8(d)] the $f^{5/2}$ states split into occupied and empty bands. In contrast to the PuN case [Fig. 6(d)] the empty $f^{5/2}$ band is not narrow but rather broad and has a two-peak structure due to the strong hybridization with Rh d states.

In Table IV (the third row corresponds to PuRh_2) the calculated values for spin, orbital, and total moments are presented. In agreement with the aforementioned density of states analysis, the Pu ion is predominantly in the f^5 configuration with a significant admixture (25%) of f^6 configuration. Large values of spin moments suggest an intermediate coupling scheme closer to LS coupling. In Table V (the third row) the values of the effective paramagnetic moments calculated using Eq. (14) are presented. The weighted value $\mu_{eff}^{calc}=1.27\mu_B$ is larger than the experimental $\mu_{eff}^{expt}=0.88\mu_B$, which still lies within the limits of $\mu_{eff}^{jj}=1.99\mu_B$ and $\mu_{eff}^{LS}=0.66\mu_B$, closer to the LS coupling value μ_{eff}^{LS}.

D. PuSi_2

The structural and magnetic properties of PuSi_2 were reported by Boulet *et al.*[101] although this phase was earlier investigated in Ref. 102. This compound crystallizes in the tetragonal ThSi_2 type (space group $I4_1/amd$) structure with $a=3.9707(3)$ Å and $c=13.6809(5)$ Å.[101] The PuSi_2 susceptibility curve shows Curie-Weiss behavior[101,103] with $p_{eff}=0.54\mu_B$, $\Theta_p=-58$ K, and $\chi_0=2.3\times10^{-5}$ emu mol^{-1}.[101] The almost field-independent resistivity shows a broad maximum at 18 K suggesting strong spin fluctuations.[101]

The LDA electronic structure [Fig. 9(a)] shows a broad deep pseudogap with a very small density of states value on the Fermi level. This pseudogap separates the $f^{5/2}$ and $f^{7/2}$ subbands [Fig. 9(b)] and the position of the Fermi level exactly in the pseudogap gave a completely filled $f^{5/2}$ band and

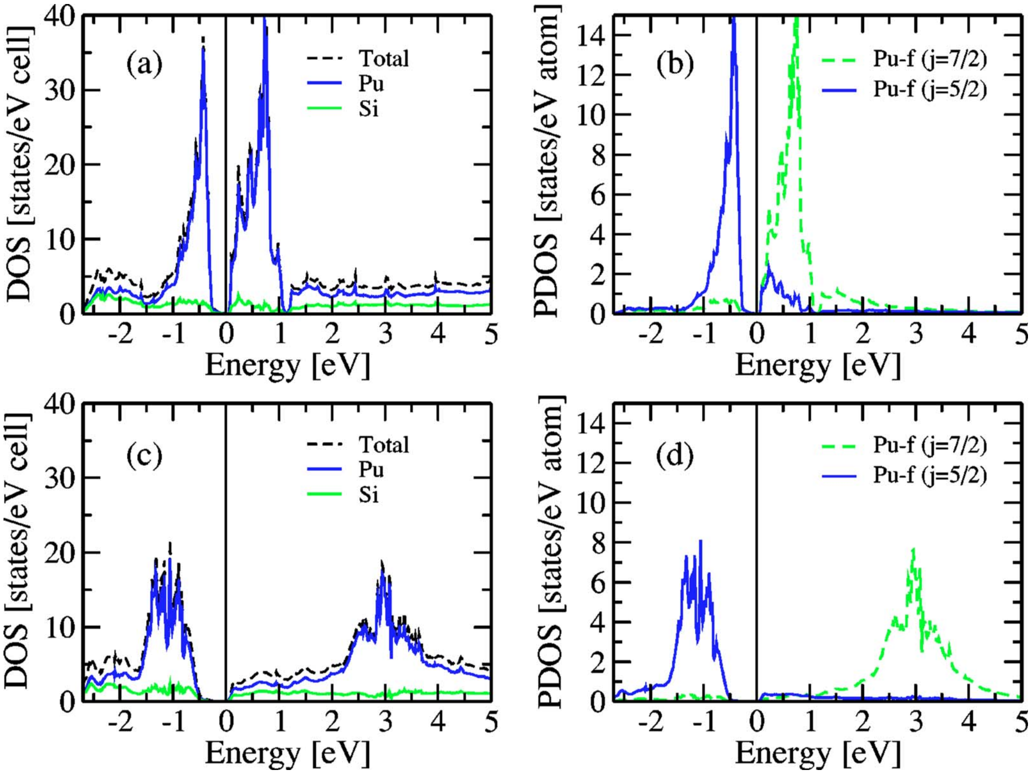

FIG. 9. (Color online) (a) Total and partial densities of states of PuSi$_2$ calculated in the LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuSi$_2$ from the LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA +U+SO.

hence a pure f^6 configuration could be expected. Indeed, the LDA+U+SO calculations gave [Figs. 9(c) and 9(d)] a solution with the same type of band structure as without the Coulomb interaction correction except for increased energy separation between $f^{5/2}$ and $f^{7/2}$ subbands.

In Table IV (the fourth row corresponds to PuSi$_2$) the calculated values for spin, orbital, and total moments are presented. The Pu ion is in nearly pure f^6 configuration with a small (5%) contribution of the f^5 configuration. The relatively small values of spin and orbital moments suggest an intermediate coupling scheme very close to pure jj coupling. The weighted value of the effective paramagnetic moment $\mu_{eff}^{calc}=0.23\mu_B$ (Table V) is smaller than the experimental $\mu_{eff}^{expt}=0.54\mu_B$.

E. PuTe

PuTe crystallizes in the NaCl-type structure with $a=6.183$ Å. The resistivity shows narrow-gap semiconductor behavior and the electronic specific heat coefficient has a high value $\gamma=60$ mJ mol^{-1} K^{-2}.[104] In another work[105] the value of $\gamma=30$ mJ mol^{-1} K^{-2} was reported. While the formal valency of Pu in PuTe is equal to +2, an intermediate valent Pu^{2+}-Pu^{3+} state in this compound was proposed.[106–109] The magnetic and optical properties of PuTe show a number of peculiarities.[110–112] A structural phase transition from the NaCl to the CsCl phase was proposed from resistivity measurements.[113]

The electronic structure of PuTe was calculated by the Dirac equation-corrected ASA,[114] relativistic LAPW,[115] and ASW LSDA.[116] From these calculations, the $f^{7/2}$ and $f^{5/2}$ subbands are split by 1 eV (Ref. 114) (or 0.3 eV in Ref. 115). The results strongly depend on the spin-orbit coupling strength.[116] Based on the Mössbauer spectra results,[117] the magnetic transition going from PuSb to PuTe with the vanishing of local moments was suggested.

The results of the LDA and LDA+U+SO calculations are presented in Fig. 10 and in Table IV (the fifth row corresponds to PuTe). The electronic structure and magnetic state are very similar to those for PuSi$_2$, only the pseudogap is not so well developed. The nearly pure f^6 configuration corresponds to the formal Pu valency +2 with small values of magnetic moments described by 30% admixture of LS coupling to the jj coupling scheme. The arguments against valency +2 in Refs. 106–109 were based on the very large ionic radius value for the Pu^{2+} ion. However, in spite of the formal configuration f^6 in our results, the total number of $5f$ electrons is equal to 5.65 (effect of the strong hybridization of $5f$ orbitals with Sb p states), which corresponds to the intermediate valency Pu^{2+}-Pu^{3+}. Another interesting fact is that on going from PuTe to PuSb the number of $5f$ electrons decreases from 5.65 to 5.16, two times smaller than expected from the formal valency difference. The very small value of magnetic moment obtained in our calculations (Table V) agrees well with a nonmagnetic state of Pu ions in PuTe.[117]

F. PuSb

From magnetization measurements and neutron experiments an antiferromagnetic spin structure was found in PuSb

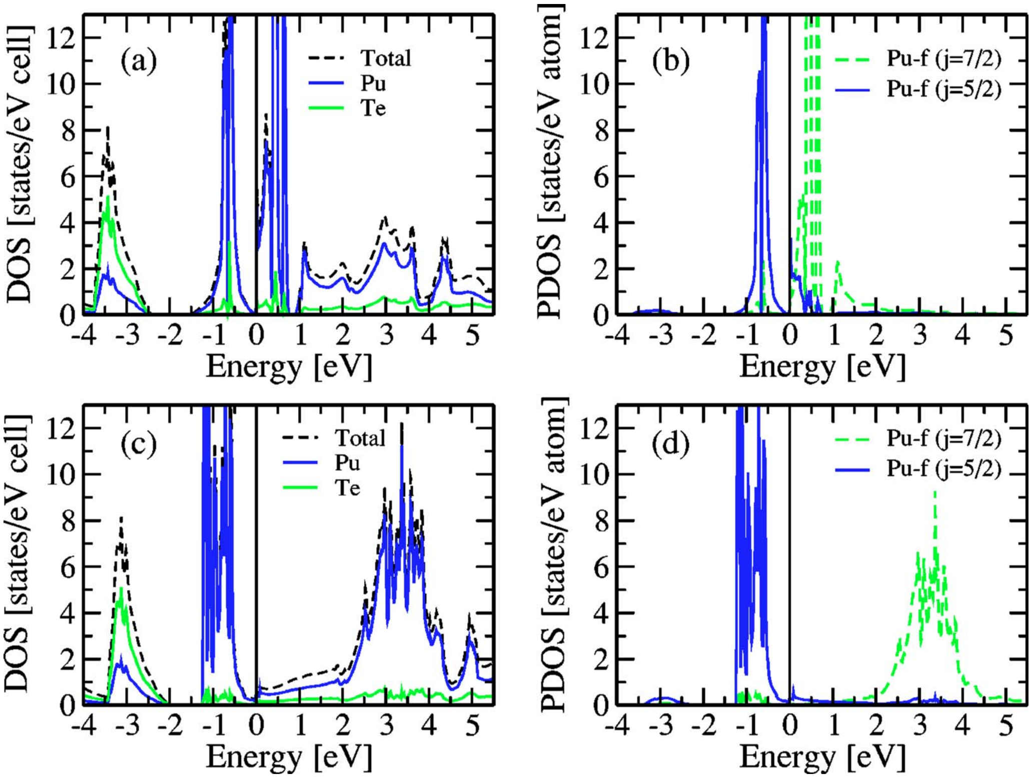

FIG. 10. (Color online) (a) Total and partial densities of states of PuTe calculated in the LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuTe from the LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

with a strong ⟨001⟩ anisotropy and ordering temperature 75 K.[118,119] A preferable intermediate coupling type closer to *LS* type was proposed in Ref. 120 (the model of a wave function consisting of 90% *LS*- and 10% *jj*-coupled wave functions[118] gave the possibility for an AFM transition, leaving strong anisotropy). The neutron diffraction experiment reveals a low-temperature Pu ion magnetic moment $\mu=0.75\mu_B$ perpendicular to the ferromagnetic (001) planes with Néel temperature $T_N=85$ K and a first-order transition to the incommensurate ferromagnetic phase.[110,120,121] The effective magnetic moment of the paramagnetic phase from susceptibility was estimated as $\mu=1.0\mu_B$.[122] A model of localized $5f$ electrons with weak hybridization to conducting electron states was proposed.[121,123] Electrical resistivity shows metallic behavior with a Kondo-like broad maximum at 106 K.[124] X-ray photoelectron spectroscopy and high-resolution valence-band ultraviolet photoelectron spectroscopy showed a strong localized nature of $5f$ Pu electrons in PuSb and a pronounced f^5 configuration.[125]

Results of the LDA and LDA+U+SO calculations are presented in Fig. 11 and in Table IV (the sixth row corresponds to PuSb). The electronic structure and magnetic state are very similar to those of PuN, according to the formal valency +2 for Pu in both compounds.

We have calculated the photoemission spectrum for PuSb (see Fig. 3). The agreement with the experimental curve[126] is rather good. The main peak at ≈1.5 eV corresponding to Pu $5f$ states [see Fig. 11(c)] is reproduced quite well.

In Table V (the sixth row corresponds to PuSb) the values of effective paramagnetic moments calculated using Eq. (14) are presented. The calculated $\mu_{eff}^{calc}=1.35\mu_B$ is close to experimental value $\mu_{eff}^{expt}=1.00\mu_B$.

V. CONCLUSION

In this work we present the results of a theoretical investigation of the Pu ion magnetic state in metallic plutonium and plutonium compounds. In contrast to all previous theoretical studies but in agreement with experimental measurements we have found for metallic Pu in both α and δ phases a nonmagnetic ground state with f^6 configuration of the $5f$ shell in the pure jj coupling scheme. The strong spin-orbit coupling for $5f$ electrons results in a splitting of the f band into a well-separated almost occupied $f^{5/2}$ subband and empty $f^{7/2}$ subband giving a preformed f^6 configuration. Taking into account the Coulomb interaction via the LDA+U potential does not change this nonmagnetic ground state.

We have shown that the approximately equal strength of spin-orbit coupling and exchange interaction, whose matrices cannot be made simultaneously diagonal in the same basis set, does not allow us to use the simplified diagonal forms of the corresponding Hamiltonian terms. That is also true for the spin-polarized potential used in the LSDA. Only a general nondiagonal matrix form of exchange interaction is appropriate for $5f$ electrons.

We have also calculated a series of plutonium compounds with different formal valencies; and the calculated magnetic moments values agree well with experimental data.

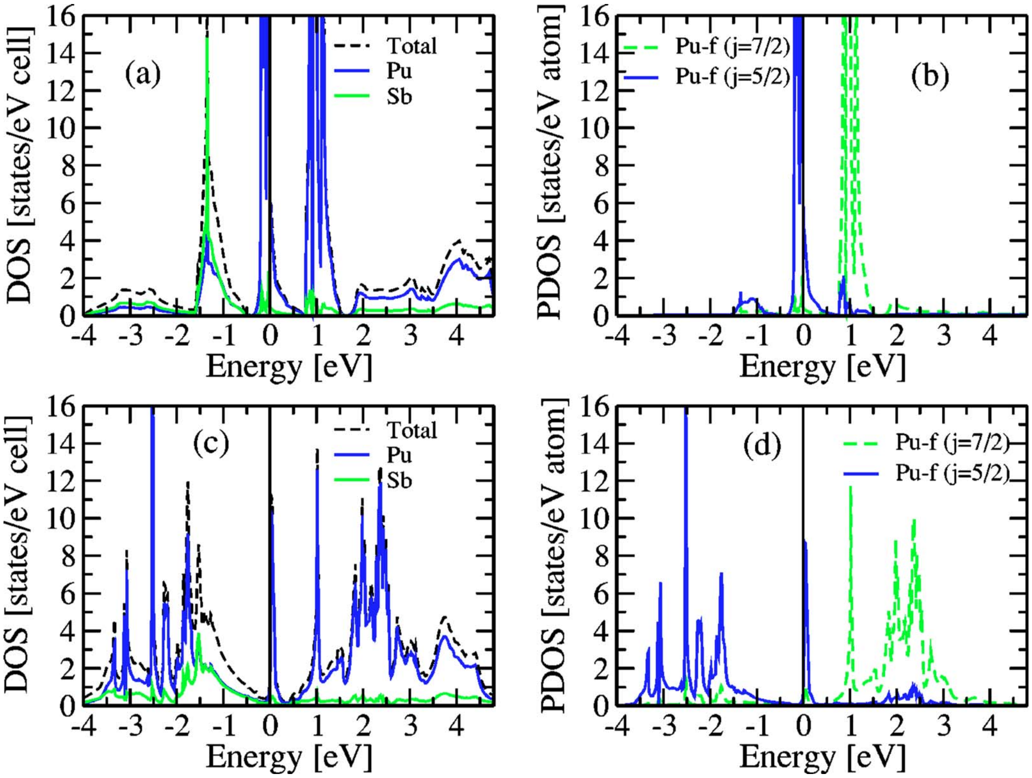

FIG. 11. (Color online) (a) Total and partial densities of states of PuSb calculated in the LDA. (b) Partial $f^{5/2}$ and $f^{7/2}$ contributions in Pu $5f$ band for PuSb from the LDA calculations. (c) The same as (a) calculated by LDA+U+SO. (d) The same as (b) calculated by LDA+U+SO.

Comparison of the calculated and experimental photoemission spectra shows that the LDA+U+SO method based on static mean-field approximation is able to reproduce Hubbard bands, but it fails to form the quasiparticle peak at the Fermi energy. The more elaborate DMFT is needed here. The results obtained in the LDA+U+SO calculations could be used as a basis for further DMFT studies.

Note added. Recently, Shick *et al.* in Ref. 127 reported a nonmagnetic ground state for δ-Pu obtained in the around-the-mean-field version of the LDA+U method.

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