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Structural, thermodynamic, and electronic properties of plutonium oxides from first principles

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We report *ab initio* calculations of the structural, electronic, optical, and thermodynamic properties of plutonium oxides (PuO_2 and β-Pu_2O_3). In order to describe the basic features of the electronic structure, a method suited to take into account strong local correlations has to be used. We apply the local density approximation/generalized gradient approximation (LDA/GGA)+U approximations to these compounds and compare them with the calculations of Sun *et al.* [J. Chem. Phys. **128**, 084705 (2008)]. Whereas a good agreement is obtained for PuO_2, our LDA and LDA+U results differ strongly from this study in the case of Pu_2O_3. In particular, the effect of the Hubbard parameter U on the volume is qualitatively and quantitatively different. Moreover, thermodynamic quantities differ. We thus focus our study on Pu_2O_3 and emphasize the importance of a careful and systematic search of the ground state in LDA+U: In particular, different hints for the occupation matrices corresponding to the electronic configurations allowed by symmetry have to be tried. This procedure is absolutely necessary to find the absolute minimum of the energy. Reliable and accurate quantitative results are given for Pu_2O_3. We thus recover a more physical behavior coherent with calculations on other systems, such as cerium oxides.

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I. INTRODUCTION

Plutonium-based materials attract much interest owing to their technological and environmental implications[1,2] as well as for theoretical prospects. PuO_2 is in particular considered as a component of nuclear reactor fuels and an important compound for the very long-term storage of plutonium. From an experimental point of view, the chemical reactivity of elemental plutonium is very complex with high and fast corrosion of the samples in various external environments. Therefore, the reactivity of plutonium metal, oxides, and hydrides has become a significant field of research in the last decade.[3–11]

As concerns theoretical calculations, the electronic structure of these correlated materials is still a challenge for electronic structure simulations. Indeed, the elemental plutonium and americium metals lie at the boundary between two electronic behaviors along the actinide row; from itinerant to localized states.[1,12–14] The early light actinides exhibit a transition metal-like behavior with f electrons contributing to the bonding. At odds, the later heavy actinides show a lanthanide-like feature with f electrons localized onto atoms. If the former behavior is well described with traditional band-structure calculations such as within DFT (density-functional theory) in the standard LDA (local-density approximation) or GGA (generalized gradient approximation), the latter is more challenging. In particular, traditional local density functional does not capture the localization effect of the f electrons coming from the strong electron-electron interaction.

In order to overcome this shortcoming, various approaches have been proposed and have been applied to plutonium and its oxides such as calculations involving self-interaction correction (SIC),[15,16] hybrid exchange-correlation functionals,[17,18] or intra-atomic Coulomb interaction (the Hubbard U parameter).[19–24] This last is the so-called DFT +U approach[25–28] and has been extensively used for a wide panel of correlated materials. A more general formalism using the combination of dynamical mean-field theory (DMFT)[29–31] with the LDA is very promising for these correlated materials.[32–35]

The phase diagram of Pu-O exhibits only two stoichiometric oxides: PuO_2 and β-Pu_2O_3. Both are insulators,[7] with, in the ionic limit, 4 and 5 f electrons. Prodan and co-workers[18] have computed with DFT and hybrid density functionals the electronic and atomic structures of these two oxides. At odds with conventional DFT calculations,[36] they found that these two compounds are insulators with an antiferromagnetic (AFM) order. These results are in good agreement with low-temperature experiments, except for the magnetic ground state of PuO_2. If PuO_2 is definitely not ferromagnetic (FM), there is still a controversy on its magnetic state. It seems to be paramagnetic (temperature independent paramagnetism[37]) but some authors argue that it could exhibit antiferromagnetic exchange.[37,38] In particular, susceptibility measurements and neutron-scattering experiments differ with results coming from crystal-field theory, and an AFM exchange between plutonium could be one solution to explain this discrepancy.[37–41]

Prodan and co-workers[17] have also established trends concerning the electronic properties of actinide dioxides along the actinide series: from ThO_2 to EsO_2. Below PuO_2, a Mott-insulator band gap is obtained,[42] whereas above AmO_2, a charge-transfer band gap takes place. The intermediate actinide dioxides PuO_2 and AmO_2 are at the crossover between the two behaviors.[17,43] They highlight the strong mixing of the actinide $5f$ and oxygen $2p$ orbitals which takes place for these two compounds.

More recently, Sun *et al.*[24] have performed calculations using the LDA/GGA+U approximations on these compounds. Even if their spectra are qualitatively coherent with Ref. 18, structural parameters do not agree in the case of Pu_2O_3. Even at the LDA level, the volume in Ref. 24 is overestimated by 7% with respect to the same LDA result in Ref. 18. In the LDA+U formalism, Sun *et al.* do find a fairly unphysical and noisy behavior for the change in volume when Hubbard correction is used. In particular, the evolution of volume with the Hubbard parameter U differs with calculations—using the same formalism—on cerium oxides which are expected to carry a similar physics.

This paper reports our results concerning the structural, electronic, optical and thermodynamical properties of the plutonium dioxide (PuO_2) and sesquioxide (β-Pu_2O_3) in the framework of the LDA/GGA+U method. We briefly describe our results on PuO_2 which are similar to the calculations of Sun *et al.*,[24] although we compute additional quantities such as fat bands and optical conductivities. The main part of the paper is devoted to solving the issue of the description of Pu_2O_3 in the LDA/GGA+U. In particular, we use symmetry argument to study possible electronic states coherent with the opening of a gap. We compare the energies of these states to find the ground state. The occurrence of several electronic metastable states is now well established[44] in LDA+U and the systematic search of the true ground state is very often necessary.[44–46] The paper is organized as follows: In Sec. II, we give the theoretical framework as well as the computational details. We describe briefly the LDA+U method. Then, we present the atomic data generated for plutonium and oxygen and test it on the Pu-δ phase of plutonium and molecular oxygen. In Sec. III, we briefly report our calculation on PuO_2 as a test of our scheme. Then, we focus on Pu_2O_3 and give a detailed account of our study: In particular, LDA and LDA+U ground state parameters (e.g., volume) strongly disagree with calculations by Sun *et al.*[24] Thermodynamic quantities in LDA+U are also different. As previously emphasized, the validity of the ground state is carefully tested: An error on the ground state would have an important effect on the energy and on thermodynamic quantities. This can be the origin of the discrepancies with the work of Sun *et al.* It seems that the authors of this paper have not studied various metastable states in order to find the absolute minimum of the energy: They could thus not have reached the ground state of the system. Thus, the main outcome of our study is to provide accurate and reliable LDA/GGA+U results for Pu_2O_3.

II. COMPUTATIONAL DETAILS

This study has been performed using the ABINIT package.[47–49] We use the projector augmented wave (PAW) formalism,[50,51] which is particularly efficient for the description of complex phases in which atomic relaxations are important. Moreover, it has the accuracy of all electron methods because the nodal structure of wave functions is correct.

A. LDA/GGA+U formalism

In this work, we have used the LDA+U framework within the PAW implementation.[46,52] The LDA+U method[25–27] has been designed from the combination of DFT+LDA and a Hubbard-type term in the Hamiltonian. The contribution to energy is the sum of the LDA energy for a given density, the electron-electron interaction term E_{ee} from the Hubbard term and a double counting term $-E_{dc}$: $E_{LDA+U}[n_{LDA+U}]=E_{LDA}[n_{LDA+U}]+E_{ee}-E_{dc}$. The last two terms are functions of the occupation matrix $n^{\sigma}_{1,2}$ in a given basis.

We used the rotationally invariant form of E_{ee} :[27]

$$E_{ee}=\frac{1}{2}\sum_{1,2,3,4}\sum_{\sigma}[\langle 13|24\rangle n^{\sigma}_{1,2}n^{-\sigma}_{3,4}+(\langle 13|24\rangle - \langle 13|42\rangle)n^{\sigma}_{1,2}n^{\sigma}_{3,4},], \quad (1)$$

where σ stands for the spin. Atom indices are neglected for clarity. $\langle 13|24\rangle$ are matrix elements of the interaction V_{ee} and are related to Slater integrals F_k (Refs. 26 and 53) and Gaunt coefficients.[27,46] The double counting term is supposed to cancel—in an approximate way—the local electron-electron interaction already described in LDA. We have chosen the "full localized limit" (FLL) double counting expression because LDA/GGA+U ground states of plutonium oxides are insulators and thus occupation of orbitals is close to one or zero. The corresponding expression is[25,27,28]

$$E^{FLL}_{dc}=U\frac{1}{2}N(N-1)-J\sum_{\sigma}\frac{1}{2}N^{\sigma}(N^{\sigma}-1). \quad (2)$$

The implementation of LDA+U in PAW (Ref. 52) in ABINIT has been described elsewhere.[46] The expression for the occupation matrix is taken from Eq. (7) of Ref. 46.

B. PAW atomic data, plutonium metal and molecular oxygen

The PAW data sets used for plutonium and oxygen are generated with the ATOMPAW code[54] with reference configurations $6s^2 6p^6 5f^4 7s^2 6d^2$ and $2s^2 2p^4$, respectively. These atomic data do not provide any overlap between neighboring PAW spheres, neither for plutonium metal and molecular oxygen nor for plutonium oxides. As concerns the exchange and correlation energy, both LDA using the Perdew-Wang parametrization[55] and the GGA using the Perdew-Burke-Ernzerhof[56] functional are employed.

Results are obtained using a plane-wave cutoff energy equal to $E_{cut}=16$ hartree for elemental plutonium, $E_{cut}=18$ hartree for the O_2 molecule, $E_{cut}=24$ hartree and 28 hartree for plutonium dioxide and sesquioxide, respectively. These input values lead to a precision lower than 1 meV/at. on total energies. The calculations on plutonium metal are performed by using a fine $12\times12\times12$ Monkhorst-Pack (M-P) mesh[57] whereas $(8\times8\times8)$ and $(5\times5\times5)$ M-P meshes are sufficient for plutonium dioxide and sesquioxide. These meshes lead, respectively, to 182, 40 and 39 **k**-points in the irreducible part of the Brillouin zone, and ensure a convergence lower than 0.3 meV per atom. In the particular case of the oxides, we have checked that using finer meshes respecting the anisotropy of the simulation cells (respectively, $16\times16\times12$ and $16\times16\times10$ for PuO_2 and Pu_2O_3) does not affect the results presented here.

As concerns the dioxygen molecule, the cohesive energy E_{coh} and the equilibrium bond length d_{eq} are listed in Table I. The cohesive energy is strongly (slightly) overestimated in LDA (GGA), in line with previous PAW calculations.[58,61,62]

In Table II, we report our results concerning plutonium metal in the Pu-δ phase. The two exchange and correlation

TABLE I. Cohesive energy E_{coh} (in Å) and equilibrium bond length d_{eq} (in Å) of the dioxygen molecule.

Method	d_{eq} (Å)	E_{coh} (eV)
LDA	1.21	7.58
GGA	1.22	6.23
LDA (Ref. 58)	1.22	7.55
GGA (Ref. 60)	1.22	6.22
Exp. (Refs. 59 and 60)	1.21	5.21

functionals as well as three possibilities for the magnetic states are studied: nonmagnetic (NM), AFM, and FM are studied. For DFT+U calculations, we choose the set of parameters used by Shick and co-workers[22] for LDA+U calculations: $U=4.00$ eV and $J=0.7$ eV. For each type of calculation, we compute the equilibrium volume V_0 and the bulk modulus B_0.

As obtained by other authors,[19–23] by using an AFM order with an appropriate couple of the Hubbard parameters, one can obtain equilibrium properties in good agreement with experiments. This is achieved in our LDA+U calculations with a theoretical equilibrium volume (25.02 Å^3) and a bulk modulus (35 GPa) close to experimental values (24.92 Å^3 and 33.9 GPa, respectively). One notices that the AFM order—which is the most stable magnetic ordering—gives better agreement with experiment than the FM order, both in DFT and DFT+U.

As we are interested in plutonium oxides we stress that the value of U for Pu may not be adequate for its oxides. Moreover, we can expect different values of U for PuO_2 and Pu_2O_3 as it has been observed for cerium oxides.[64] Lastly, one also has to keep in mind that the value of the screened interaction U can be dependent of the exchange and correlation functional (see, for example, Ref. 64). A better solution would nevertheless be to compute U from first principles for each system.

C. Ground state and convergence of the self-consistent field

Note that the reader only interested in physical properties of plutonium oxides could skip this technical section where we explain the procedure used to find out the ground state in our calculations. Indeed, this one is hard to determine for systems with strong electron-electron correlations and partially filled open shells. A large number of local minima corresponding to various occupation matrices[44–46] can prevent the self-consistent calculation of density to find the global minimum and thus can lead to spurious ground states. It is especially important here, since all the bare f levels are located in the same range of energy, and thus, different filling of these levels are in competition. These drawbacks are related to these peculiar systems and to the use of a method which takes into account strong correlations. They are not specific to the LDA/GGA+U method: They also appear for SIC or hybrid functional calculations.[65,66]

To find the true ground state among all the local minima, we have to compare the energies of each of these. In practice, in order to stabilize these local minima—including the global one—we introduce several occupation matrices as starting points of the calculation [see, e.g., Eq. (1)]. Technically, we fix the occupation matrix during the LDA+U part of the Kohn-Sham potential in ten electronic steps. It thus shifts upward empty orbitals and downward filled orbitals in a way coherent with the imposed occupation matrix. Then, the constraint is released until convergence of the self-consistent field. This procedure improves greatly the numerical convergence and allows for a systematic study of all states coherent with a given symmetry.

From a physical point of view, we expect the LDA/GGA+U formalism to open a gap and split the f levels into occupied and filled states. Actually, we found this situation more energetically stable in LDA/GGA+U with respect to the metallic case. In order to obtain an insulator, degenerate orbitals have to be totally filled or empty: Indeed, a partially filled situation would correspond to a metal.[44] For example, in both antiferromagnetic PuO_2 and Pu_2O_3, the f levels are split in two twofold degenerate levels and three nondegenerate levels. The filling of these orbitals will depend on the number of available electrons.

In the case of Pu_2O_3, each plutonium carries 5 f electrons. The space group of Pu_2O_3 is $P\bar{3}2/m1$ and the point group for Pu is D_{3d}: f orbitals thus split in five irreducible representations (E_u, E_u, A_{2u}, A_{2u}, and A_{1u}). We thus found five possibilities for an electronic configuration coherent with the opening of a gap among f orbitals: (i) Two with the two twofold degenerate levels filled with four electrons. Intuitively, three possibilities were expected, corresponding to the filling of each of the three nondegenerate levels by the remaining electron. However, it appears that the coupling of the two A_{2u} levels forbids the stabilization of one of them.

TABLE II. Equilibrium volume V_0 (in Å^3) and Bulk modulus B_0 (in GPa) of the δ-Pu phase of plutonium.

Method	V_0 (Å^3)			B_0 (GPa)		
	NM	FM	AFM	NM	FM	AFM
LDA	16.39	19.17	19.74	208	66	80
GGA	17.77	27.40	23.54	156	32	53
LDA+U		26.32	25.02		45	35
GGA+U		32.32	31.16		34	30
Exp. (Ref. 63)		24.92			33.9	

(ii) Three with all the nondegenerate levels filled. Intuitively, two possibilities were expected, corresponding to the filling of each of the two twofold degenerate levels for the two last electrons. However, it appears that the coupling of the two E_{2u} levels enables the stabilization of a supplementary possibility.

The global minimum is found by direct comparison of their energies: It corresponds to the filling of the four orbitals belonging to the two irreducible representations E_u (f^{2-},f^{2+},f^{1-},f^{1+}) and to the filling of the nondegenerate level corresponding to f^{3+} (and belonging to A_{1u}). We have used the notation of Refs. 46 and 67 for the f orbitals. This thorough search makes us confident about the reliability of the ground state.[68]

Sun *et al.*[24] do not mention the occurrence of metastable states nor the occupancy of the ground state. It is thus likely that the calculations presented in this paper do not correspond to the ground state of the system: This could explain some of the discrepancies with our work.

In the case of PuO_2, we find that the ground state corresponds to the occupation of a doubly degenerate state and two nondegenerate states. We have also noticed that occupation matrices for AFM and FM ground states are equal for a given atom. Thus, starting from the FM occupation matrix, we only have to invert the up and down spins for atoms linked by an antiferromagnetic symmetry operation to recover the AFM occupation matrix.[46] It shows that the difference of energy between different occupation matrices—which is linked to crystal field, hybridization or spin-orbit coupling—is larger than the energy due to the interaction between spins on different atoms.

Finally, in order to constrain the AFM or FM orders during the SCF minimization, we impose the corresponding magnetic space group. In addition, for the AFM order, we use the Shubnikov space group to fix the symmetry. These constraints, added to the previous ones, improve strongly the convergence cycle of magnetic systems.

III. RESULTS

A. Crystallographic data

The phase diagram of plutonium oxides shows, respectively, the monoxide PuO, the sesquioxide Pu_2O_3 and the dioxide PuO_2, when the chemical potential of oxygen increases. Recently, an intense discussion has attracted much interest about a higher composition plutonium dioxide PuO_{2+x}.[15,18,69,70]

At room temperature and zero pressure conditions, the stoichiometric plutonium dioxide crystallizes in the fluorite structure with a $Fm3m$ space group. In the cubic unit cell (defined by the lattice parameter a_0) the crystallographic positions are Pu(0,0,0), $O_I(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $O_{II}(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. At higher pressure (39 GPa experimentally[71]) a $PbCl_2$ structure (space group *Pnma*) takes place. PuO_2 is proved to be an insulator with a conductivity band gap which is equal to 1.8 eV.[72] This compound is definitely not ferromagnetic and it has been argued that antiferromagnetic exchange could explain[37,38] the discrepancy between neutron-scattering experiments[41] and magnetic susceptibility measurements.[39]

Concerning the plutonium sesquioxide, two nonstoichiometric phases with cubic unit cells (α and α'-Pu_2O_3) exist. We focus on the stoichiometric β phase which crystallizes in a hexagonal structure (defined by the a_0 and c_0 lattice constants). The crystallographic positions are Pu$(\frac{1}{3},\frac{2}{3},\pm z_{Pu})$, $O_I(0,0,0)$ and $O_{II}(\frac{1}{3},\frac{2}{3},\pm z_O)$, with $(z_{Pu};z_O)$ a couple of internal parameters. This compound is insulating, even if no experimental value for the gap is available to our knowledge, and an AFM order—in which the magnetic unit cell is the same as the chemical unit cell—is experimentally observed below 4 K.[73]

In the following, we will consider the two stoichiometric plutonium oxides: PuO_2 and β-Pu_2O_3 (which will be shortened to Pu_2O_3 for simplicity). As the LDA+U formalism implies most often the creation of a magnetic ordering, we have described PuO_2 both with a FM and an AFM order. We have considered two types of AFM ordering for which the stacking sequence of planes of opposite magnetic moment is along the [100] and [111] directions of the fluorite structure. In both cases, the magnetic moments of each plutonium atom lying in the (100) and (111) planes are identical. We found that these two magnetic orderings are nearly degenerated with an energy difference in the range of the precision of our calculations. Thus we have chosen to consider only the first above mentioned magnetic structure in the following. At odds, for Pu_2O_3, we consider only the primitive unit cell which is sufficient to describe the experimental AFM order below 4 K.

B. Atomic and electronic structure of PuO_2

We report in Table III the volumes V_0, bulk moduli B_0 and gap values Δ obtained in the frameworks of LDA, GGA, LDA+U and GGA+U calculations. Volumes and bulk moduli are obtained by fitting the *ab initio* 0 K equation of state to the Birch-Murnaghan one. All these results are very close to the ones published by Prodan *et al.*[18,74] and more recently by Sun and co-workers.[24] We found an overall agreement, both quantitatively and qualitatively, for the magnetic properties, the electronic properties, as well as the structural ones. In particular, we recover the main conclusion of these two studies: Standard DFT fails to describe an insulating ground state for PuO_2 (see the top panel on the left-hand side of Fig. 1).

Densities of states are provided in Fig. 1. They reproduce all the features included in the works of Prodan *et al.*[18] and of Sun *et al.*[24] In addition, the band structure of the tetragonal antiferromagnetic PuO_2 is shown in Fig. 2, with the indication of the character of the orbitals: These fat bands show unambiguously that individual bands have a mixed O-p and Pu-f character. With a typical value of U=4.0 eV, we find a band gap of, respectively, 2.1 and 2.2 eV within LDA+U and PBE+U formalisms (see Fig. 1). We cannot expect a good agreement with the experimental conductivity gap since it contains two particle excitations. Note that hybrid functional calculations lead to a larger gap by 0.9 eV in HSE and by 1.6 eV in PBE0 (see Table III). Both LDA+U and PBE+U formalisms lead to an AFM ground state with a net magnetic moment on plutonium atoms of around 3.9 μ_B

TABLE III. Equilibrium properties of PuO_2 and Pu_2O_3. Structural parameters (V_0 and B_0) as well as band-gap energy (Δ), spin moments ($\mu_{mag.}$) and total-energy differences (E_{FM}-E_{AFM}) are reported for four approximations of the exchange and correlation functional: LDA, PBE, LDA+U, and PBE+U. In addition, we also show experimental (Exp.) and results obtained by Prodan *et al.* (Refs. 18 and 74) and Sun *et al.* (Ref. 24). All these results are obtained performing a complete relaxation of the geometry. DFT+U calculations are performed with the same set of (U,J) parameters as for plutonium metal: U=4.0 eV and J=0.7 eV (0.75 eV in Ref. 24). Values of Sun *et al.* are extracted from curves of Ref. 24.

Compound	Method	Magnetism	V_0 (Å^3)	B_0 (GPa)	Δ (eV)	E_{FM}-E_{AFM} (meV)	$\mu_{mag.}$ (μ_B)
PuO_2	LDA	FM	36.57	231	0.0	−285	3.81
	PBE	FM	39.06	190	0.0	−276	3.96
	LDA+U	AFM	38.03	232	2.1	19	3.80
	PBE+U	AFM	40.34	199	2.2	14	3.89
	LDA+U [a]	AFM	38.50	208	1.7	>0	
	GGA+U [a]	AFM	40.92	184	1.7	>0	
	LDA[b]	FM	36.76	229	0.0	−310	
	PBE[b]	FM	39.34	189	0.0	−259	
	PBE0[b]	AFM	39.04	221	3.4	14	
	HSE[b]	AFM	39.28	220	2.7	14	
	Exp.		39.32[c]	178[d]	1.8[e]		
Pu_2O_3	LDA	FM	68.13	166	0.0	−127	4.40
	PBE	FM	73.43	131	0.0	−219	4.59
	LDA+U	AFM	71.51	124	1.1	18	4.68
	PBE+U	AFM	78.08	110	1.7	4	4.74
	LDA[a]	AFM	75.75		0.0	<0	
	GGA[a]	AFM	70.50		0.0	<0	
	LDA+U [a]	AFM	76.60		2.0	>0	
	GGA+U [a]	AFM	76.60		2.2	>0	
	Exp.[f]		75.49–76.12		>0	>0	

[a] Reference 24.
[b] References 18 and 74.
[c] Reference 69.
[d] Reference 75.
[e] Reference 72.
[f] References 73 and 76.

which is not so far from the complete ionic limit of 4 μ_B.

The main difference between our results and the ones of Sun *et al.* relies on the evolution of V_0 vs U (see Fig. 3). This evolution is typical of what is expected, i.e., an increase in V as a function of U both for LDA+U and PBE+U calculations. This result can be easily understood since increasing the localization of the f electrons tends to decrease the cohesion of the crystal and then to increase the lattice parameter. Sun *et al.* report the same trend but the amplitude of the variation of the volume is higher in their study. This difference can be attributed either to the type of exchange and correlation functional used and/or to differences in the spatial extension of the PAW atomic data used.

C. Atomic and electronic structure of Pu_2O_3

The conclusions arising from our study of the PuO_2 compound are in close agreement with the ones published by Prodan *et al.*[18,74] and Sun and co-workers.[24] We will see in the following that this overall agreement is strongly affected when dealing with the sesquioxide Pu_2O_3.

As the Pu_2O_3 compound crystallizes in a structure which has a hexagonal symmetry with two internal parameters (z_{Pu} and z_O), a proper study of its physical properties implies to perform a complete structural relaxation. This has not been done by Prodan *et al.* who have restricted their calculations to the experimental geometry by fixing the three parameters c/a, z_{Pu}, and z_O to their corresponding experimental values. On the other hand, Sun and co-workers do not clearly mention if such a complete structural relaxation has been done.

We have chosen to relax all the degrees of freedom of the Pu_2O_3 unit cell starting from the experimental geometry given in Refs. 73, 76, and 77. We first discuss the physical properties obtained for the experimental geometry as done by Prodan. These are reported on Table IV where they are compared with the values published by Prodan *et al.*[18,74] Both our LDA and GGA volumes are in quasi-perfect agreement with the corresponding ones of Prodan and co-workers.

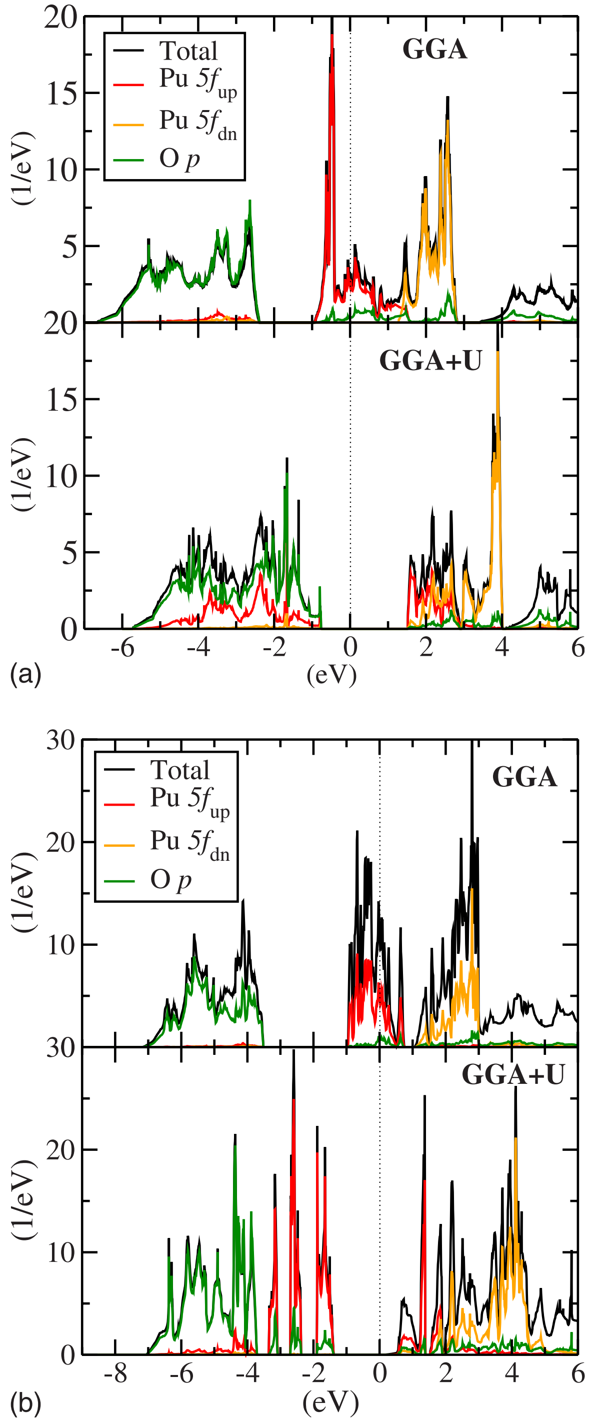

FIG. 1. (Color online) Total and projected density of states of PuO_2 (a) and Pu_2O_3 (b) computed for the ground states in the GGA and GGA+U. The Fermi energy stands at 0 eV.

There is also a close agreement for the bulk moduli and like Prodan *et al.* we find a wrong FM metallic ground state within the DFT. This validates our scheme and our further calculations for relaxed geometries. At odds with standard DFT calculations, the ones performed in the LDA/GGA+U frameworks are consistent with the AFM insulating state observed experimentally.

Let us move on to the results which concern the relaxed structures calculated within both the LDA and LDA+U frameworks. The corresponding structural parameters as well as the electronic and magnetic properties are given in Tables III and V. The complete geometry relaxation of Pu_2O_3 shows that the lattice parameter a_0 slightly decreases in DFT and increases in DFT+U. The opposite behavior is observed concerning the c/a ratio. Thus it appears that, after relaxation,

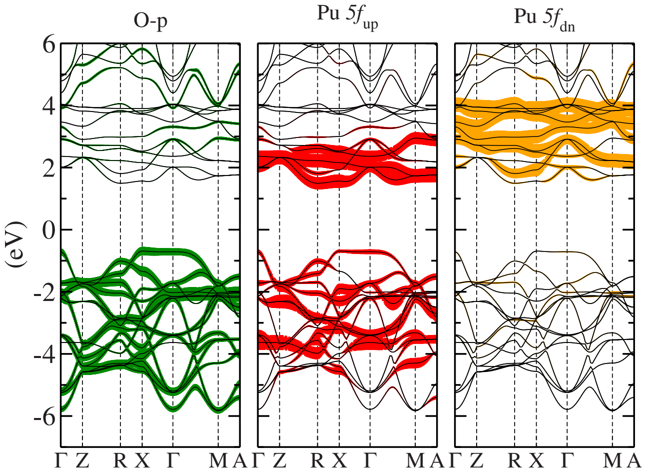

FIG. 2. (Color online) Band structure of the tetragonal antiferromagnetic PuO_2, in GGA+U. Fat bands are used to show the projection of Kohn-Sham functions on O-p, Pu-$f_\uparrow$, and Pu-$f_\downarrow$ orbitals.

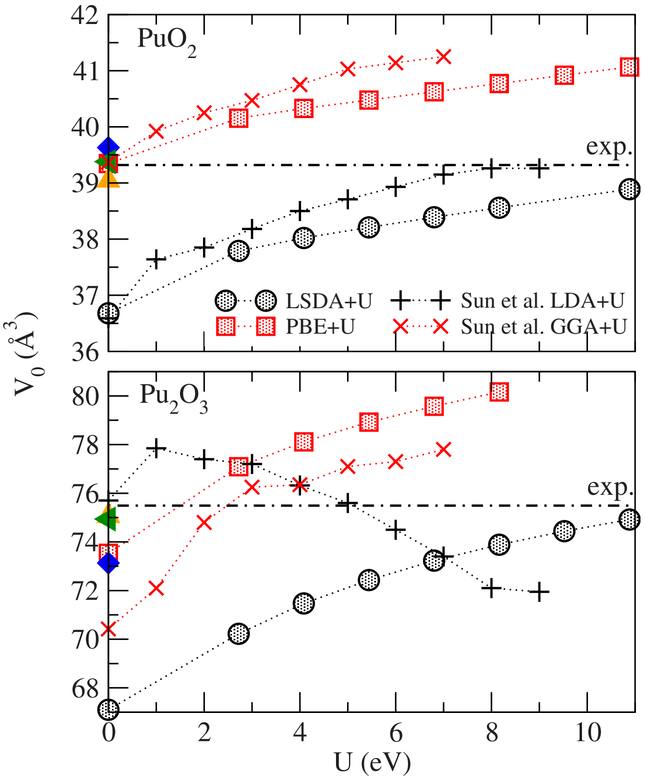

FIG. 3. (Color online) Calculated equilibrium volumes for PuO_2 and fully-relaxed Pu_2O_3 in LSDA+U and GGA+U as a function of the parameter U. The blue diamond, orange up triangle and green left-pointing triangle are, respectively, PBE, PBE0 and HSE results from Prodan *et al.* (Ref. 18).

TABLE IV. Equilibrium properties of β-Pu_2O_3 for a fixed lattice parameter ratio $a_0/c_0=0.64468$ which is the experimental measurement by Flotow and Tetenbaum (Ref. 77). Structural parameters a_0, B_0 as well as band-gap energy (Δ) or magnetic properties (corresponding to the total-energy differences E_{FM}-E_{AFM}) are reported for four approximations of the exchange and correlation functional: LDA, PBE, LDA+U, and PBE+U. DFT+U calculations are performed with the same set of Hubbard parameters as for plutonium metal: $U=4.0$ eV and $J=0.7$ eV. We compare our results with the ones published by Prodan and co-authors who have performed calculations for the same a_0/c_0 ratio (Ref. 74).

Method	a_0 (Å)		B_0 (GPa)		Δ (eV)		E_{FM}-E_{AFM} (meV)
	FM	AFM	FM	AFM	FM	AFM	
LDA	3.701	3.686	187	176	0.0	0.0	−166
PBE	3.793	3.790	149	142	0.0	0.0	−264
LDA+U	3.786	3.784	166	164	0.4	1.06	14
PBE+U	3.879	3.879	138	137	1.04	1.65	3
LDA[a]	3.690	3.680	181	175	0.0	0.0	−185
PBE[a]	3.790	3.791	146	136	0.0	0.0	−291
PBE0[a]	3.823	3.824	176	175	2.51	3.50	11
HSE[a]	3.823	3.822	159	158	1.83	2.78	3

[a] References 18 and 74.

the equilibrium volumes remain almost constant. Whereas this one is strongly underestimated by −10% in LDA and more slightly by −3% in GGA, the values in LDA+U and GGA+U calculations surround the experimental equilibrium volume and deviate by only −5% and +3%. Internal parameters (z_{Pu};z_O), band-gap values Δ and total-energy differences (E_{FM}-E_{AFM}) are not affected by relaxations. In particular, for the LDA/GGA+U calculations, the AFM order remains the most stable and the ground state is still insulating. We can notice that, in the AFM order, the bulk modulus is softened and decreases from 164 and 137 GPa to 124 and 110 GPa in LDA+U and GGA+U, respectively (see Table III).

In this paragraph, we discuss the results of Sun *et al.*[24] Even if they do not give the internal parameters z_{Pu} and z_O used in their calculations for the Pu_2O_3 compound, they give the equilibrium lattice parameter a_0 and the equilibrium volume V_0 of the AFM state. We can thus deduce their c_0/a_0 ratio. First we discuss the DFT results. It appears that their volume is overestimated by 13% in LDA and underestimated by 4% in GGA with respect to our results which are validated by comparison to results of Prodan (see above). Thus we do think that the reliability of the results published by Sun *et al.* for Pu_2O_3 already at the LDA/GGA levels is questionable. Moreover, it appears really unexpected to find a GGA volume lower than the LDA one.

This feeling is confirmed when we look at their DFT+U calculations. Indeed, in Fig. 3 where we plot the evolution of V_0 vs U, it appears that the curves obtained by Sun *et al.* are very noisy (note that the noise does not come from our data extraction since it is already present in their original curves[24]) which certainly comes from convergence problems. In our DFT+U calculations we have carefully checked that we converge to the proper ground state at each point of our curves by using the technique described in Sec. II C. That leads to very smooth curves as expected. However the most surprising result of Sun *et al.* is that they predict a decrease in V_0 when increasing the value of U in LSDA+U. They

TABLE V. Equilibrium properties of the fully-relaxed β-Pu_2O_3 compound. Structural parameters [a_0, B_0, c/a and (z_{Pu};z_O)] are reported for four approximations of the exchange and correlation functional: LDA, PBE, LDA+U, and PBE+U. DFT+U calculations are performed with the same set of (U,J) parameters as for plutonium metal: $U=4.0$ eV and $J=0.7$ eV.

Method	a_0 (Å)		c/a		(z_{Pu};z_O)	
	FM	AFM	FM	AFM	FM	AFM
LDA	3.689	3.629	1.567	1.621	(0.2410;0.6414)	(0.2388;0.6390)
PBE	3.764	3.718	1.590	1.652	(0.2436;0.6417)	(0.2425;0.6426)
LDA+U	3.845	3.849	1.457	1.448	(0.2373;0.6535)	(0.2372;0.6548)
PBE+U	3.905	3.905	1.514	1.514	(0.2433;0.6482)	(0.2439;0.6484)
Exp.[a]	3.838		1.542		(0.2422;0.6489) (0.2408;0.6451)	

[a] References 73 and 76.

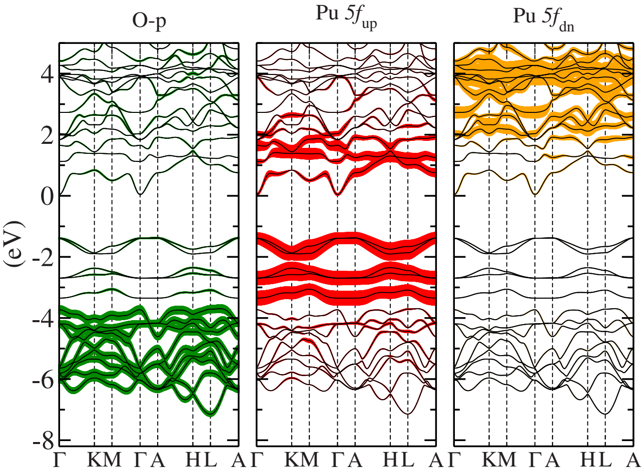

FIG. 4. (Color online) Band structure of the antiferromagnetic Pu_2O_3, in GGA+U. Fat bands are used to show the projection of Kohn-Sham functions on O-p, Pu-$f_\uparrow$, and Pu-$f_\downarrow$ orbitals.

agree that this behavior is quite uncommon and argue that it may come from a sensitivity of the anisotropy in Pu 5*f* orbitals to the treatment of the exchange-correlation potential because within a GGA+U approach they found the completely opposite behavior. Our simulations performed at LDA+U and PBE+U levels both describe an increase in the equilibrium volume when increasing U. Note that this result is clearly expected since the localization of the Pu 5*f* electrons is raised in this case and consequently they participate less and less to the bonding which naturally leads to increase the volume. We assume that the large discrepancies between our DFT+U results and the ones of Sun *et al.* could be due to the fact that the latter had not converged to the proper ground states. That could explain the nonmonotonic dependence of V_0 vs U observed in their work. Indeed, among the five density matrices tested, we found one metastable state for which the calculated density of states (DOS) was very similar to the one published by Sun and co-workers. In particular, it also exhibits three 5*f* peaks, the first two being very close while the third one is more separated from the others. In this metastable state, the total width of these 5*f* peaks is around 1.7–1.8 eV and the band gap on the order of 2 eV like what can be seen on the GGA+U DOS of Sun *et al.*[24] However we stress that this state was 165 meV (per unit formula of Pu_2O_3) higher in energy than the ground state. It is thus possible that the electronic states might be different in both studies and that Sun *et al.* did not converge to the most stable one.

Let us now discuss the DOS in detail. Contrary to PuO_2, we can see in Figs. 1 and 4 that Pu_2O_3 exhibits a separation between Pu-5*f* and O-2*p* states (see Fig. 1), within the upper part of the valence band—a lower Hubbard band composed of three narrow Pu-5*f* peaks and an O-2*p* valence band below. Pu_2O_3 is thus a Mott Hubbard insulator. In this case, both the Pu-5*f* and Pu-5*d* form the conduction band. The plot of the fat bands in Fig. 4 gives in this case the same information concerning the weaker hybridization between O-*p* and Pu-*f*. This result is in good agreement with previous hybrid functional calculations performed by Prodan *et al.*[18,74] and recent photoelectron spectroscopy (PES) experiments.[7,78] However, contrary to hybrid functional calculations, three peaks rather than one compose the present upper valence band (of Pu-*f* character) just below the Fermi level. This feature leads to an overall bandwidth of 2 eV which is more in line with the experimental width (3 eV[78]) than the hybrid functional calculations (1 eV). The width of the oxygen bands (3.5 eV) is coherent with experimental width (3.5 eV) and hybrid functional calculation (3.5 eV).

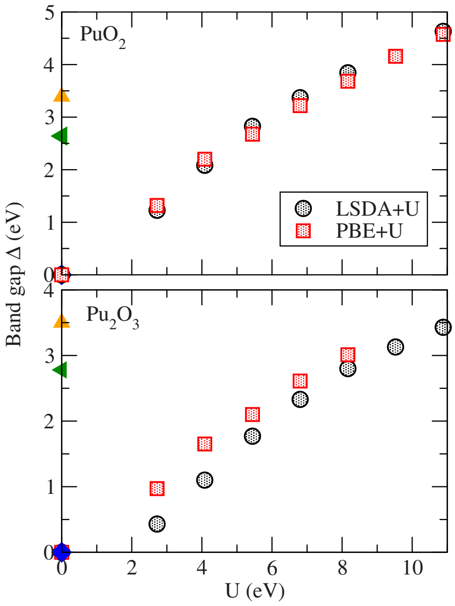

FIG. 5. (Color online) Calculated band gap for Pu_2O_3 in its ground state as a function of the parameter U. The blue diamond, orange up triangle and green left-pointing triangle are, respectively, PBE, PBE0 and HSE results from Prodan *et al.* (Ref. 18). The LDA+U and GGA+u results of Sun *et al.* (Ref. 24) are, respectively, given by the plus and cross symbols.

In Fig. 5, we compare our calculated band gaps vs U with the results of Sun and co-workers. Within LDA+U, we predict smaller gaps than within GGA+U, in agreement with Sun and co-workers. However our values are very much smaller than theirs. As discussed before, it may come from the fact that Sun *et al.* used wrong ground states with larger gaps.

D. Optical properties of plutonium oxides

The optical conductivity and reflectivity of PuO_2 and Pu_2O_3 are plotted in Fig. 6. Experimental data are not available. The optical conductivity is computed with the Kubo-Greenwood formalism. Technical details of the implementation are described in Ref. 79. There conductivity equals zero for a frequency lower than the value of the band gap (hole-electron interactions during the excitation are neglected here). For PuO_2, two peaks are observed at 7 eV and 10 eV. These two peaks come mainly from transition to, respectively, *f* states at the bottom of the conduction band and 5*d* states. The increase in the conductivity beyond 16 eV is due to transition from 2*s* states of oxygen and semicore states to conduction band. For Pu_2O_3, the same effect is observed.

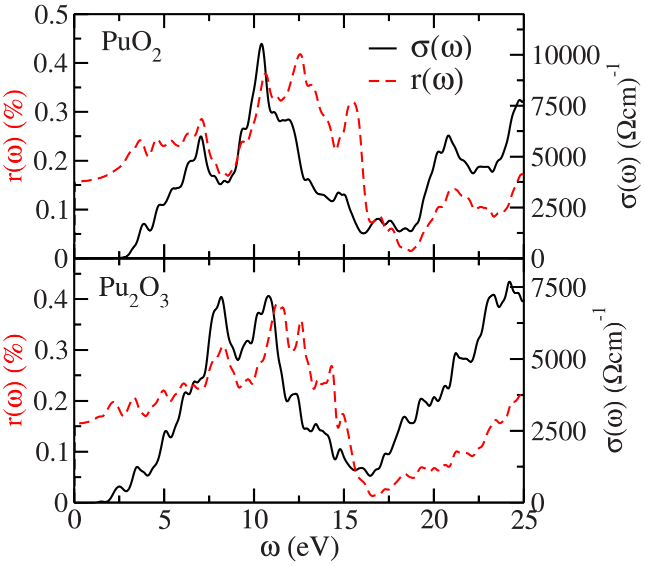

FIG. 6. (Color online) Real part of the optical conductivity and reflectivity of PuO$_2$ (up) and Pu$_2$O$_3$ (down), computed in the GGA+U approximation with $U=4$ eV. The smearing is 0.2 eV.

The main peaks are located at 8 eV and 11 eV. Using Kramers-Kronig relation, and relations between response function, one can obtain the reflectivity (shown on the same graph). Reflectivity for PuO$_2$ at $\omega=0$ is not far from the value obtained experimentally for UO$_2$,[80] whose experimental gap (2.1 eV) is near our theoretical value for PuO$_2$.

E. Thermodynamic properties

At last, we also compute the formation energies E_f of PuO$_2$ and Pu$_2$O$_3$ with respect to molecular oxygen and Pu-δ. These energies, related to the Pu+O$_2$→PuO$_2$ and $2\text{Pu}+\frac{3}{2}\text{O}_2\rightarrow\text{Pu}_2\text{O}_3$ reactions, can be written as follows:

$$E_{\mathrm{f}}^{\mathrm{PuO_2}} = E_{\mathrm{tot}}^{\mathrm{PuO_2}} - E_{\mathrm{tot}}^{\mathrm{Pu}} - E_{\mathrm{tot}}^{\mathrm{O_2}}, \tag{3}$$

$$E_{\mathrm{f}}^{\mathrm{Pu_2O_3}} = E_{\mathrm{tot}}^{\mathrm{Pu_2O_3}} - 2E_{\mathrm{tot}}^{\mathrm{Pu}} - \frac{3}{2}E_{\mathrm{tot}}^{\mathrm{O_2}}, \tag{4}$$

with $E_{\mathrm{tot}}^{\mathrm{PuO_2}}$, $E_{\mathrm{tot}}^{\mathrm{Pu_2O_3}}$, $E_{\mathrm{tot}}^{\mathrm{O_2}}$, and $E_{\mathrm{tot}}^{\mathrm{Pu}}$ as the total energies of the PuO$_2$ and Pu$_2$O$_3$ compounds, of molecular oxygen and Pu-δ phase, respectively. The energy of reaction for the oxidation of Pu$_2$O$_3$, $\text{Pu}_2\text{O}_3+\frac{1}{2}\text{O}_2\rightarrow 2\text{PuO}_2$, is also computed as

$$E_{\mathrm{r}}^{\mathrm{Pu_2O_3\rightarrow PuO_2}} = 2E_{\mathrm{f}}^{\mathrm{PuO_2}} - E_{\mathrm{f}}^{\mathrm{Pu_2O_3}}. \tag{5}$$

All these results are listed in Table VI. Whereas in LDA calculations formation energies deviate from experiments by 5 and 2% for PuO$_2$ and Pu$_2$O$_3$, in LDA+U ones these differences increase up to 11 and 8%, respectively. If the introduction of the on-site Coulomb repulsion damages the results obtained with LDA calculations, this one improves the GGA results for PuO$_2$ and Pu$_2$O$_3$.

The larger formation energies of PuO$_2$ and Pu$_2$O$_3$ found in LDA with respect to GGA are coherent with the overbinding usually found in the LDA approximation. For the same reason, the reaction of oxidation of Pu$_2$O$_3$ is more exothermic in LDA(+U) than in GGA(+U). The LDA overestimation is larger in PuO$_2$ which involves a more important number of Pu-O bonds.

TABLE VI. Formation energies E_{f} of PuO$_2$, Pu$_2$O$_3$ and oxidation of Pu$_2$O$_3$ for four approximations of the exchange and correlation functional: LDA, GGA, LDA+U, and GGA+U. DFT+U calculations are performed with the same set of (U,J) parameters as for plutonium metal: $U=4.0$ eV and $J=0.7$ eV. In this Table, f.u. stands for formula unit and the following conversion factor is also used for experimental data: 1 eV/at=23.061 kcal/mol.

	E_{f} (eV/f.u.)		E_{r} (eV/Pu$_2$O$_3$)
Method	PuO$_2$	Pu$_2$O$_3$	$\text{Pu}_2\text{O}_3+\frac{1}{2}\text{O}_2\rightarrow 2\text{PuO}_2$
LDA	−10.88	−16.66	−5.10
GA	−9.70	−15.34	−4.06
LDA+U	−11.46	−17.74	−5.18
GGA+U	−10.14	−16.18	−4.10
Exp. (Ref. 1)	−10.36	−16.40	−4.32

The removal of the LDA/GGA overbinding of the oxygen molecule (see Table I) in these formation energies makes these reactions more exothermic. Concerning the reaction of oxidation of Pu$_2$O$_3$, the good agreement of GGA/GGA+U with experimental results is nearly unchanged by this correction whereas corrected LDA/LDA+U energies are more negative.

At last, we also show in Fig. 7 the variation of the $\text{Pu}_2\text{O}_3+\frac{1}{2}\text{O}_2\rightarrow 2\text{PuO}_2$ reaction energy as a function of U. The variation of the energy of reaction of oxidation of Pu$_2$O$_3$ with U is similar to what is observed in cerium oxides[58,64] (see Fig. 7). We checked that this linear variation (for $U>0$) comes almost completely from the terms in the energy that depend explicitly on U (i.e., $E_{\mathrm{ee}}-E_{\mathrm{dc}}$, see Sec. II A). As emphasized before,[58,81] this behavior depends on the choice of local orbitals on which LDA+U is applied. A way to correct this has been proposed by Pethukov *et al.*[82]

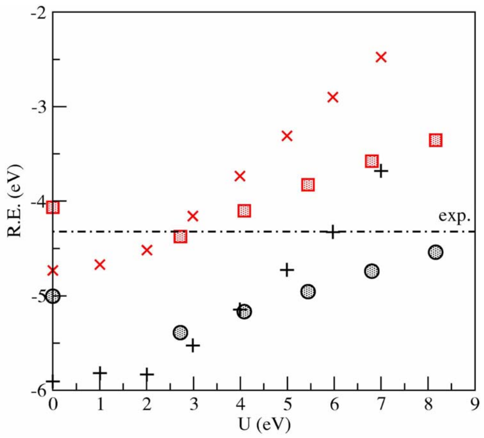

FIG. 7. (Color online) Calculated energy of the reaction $\text{Pu}_2\text{O}_3+\frac{1}{2}\text{O}_2\rightarrow 2\text{PuO}_2$ versus the value of U. In black, LSDA+U results and in red, GGA+U ones. The results of Sun *et al.* (Ref. 24) are, respectively, given by the plus and cross symbols. We have shifted their values by their estimation of the DFT-induced O$_2$ overbinding.

Comparing our calculated reaction energies with the ones published by Sun *et al.* (for the sake of coherence, we have shifted their values by their wrong estimation[83] of the overbinding of the O_2 molecule given by the DFT) we can see that they both follow the same trend vs U. The increase in the Pu_2O_3 oxidation reaction energy is more important in the work of Sun and co-workers. We have mentioned the same tendency for the evolution of V_0 vs U and the cause is probably the same.

IV. CONCLUSION

The structural, electronic, optical and thermodynamic properties of the PuO_2 and Pu_2O_3 compounds are evaluated by means of *ab initio* calculations. Within the standard DFT framework, we recover the previously published results of Prodan *et al.*[18,74] for these two oxides. We are thus quite confident in both our PAW atomic data sets and our numerical scheme. Even if DFT, especially in the GGA, allows a nice description of the structural properties of these Pu compounds, it clearly fails to capture all other properties. In order to overcome this shortcoming, we use the LDA/GGA+U framework: a method suited to take into account strong local correlations.

In the case of PuO_2, our LDA/GGA+U results are very close to the ones recently published by Sun *et al.*[24] A fairly good agreement is also obtained with the hybrid functional calculations of Prodan and co-workers.

However, we find strong discrepancies with the work of Sun *et al.* for the plutonium sesquioxide while our results still agree with the hybrid functional study of Prodan. Facing this problematic disagreement, we focus our attention on the Pu_2O_3 oxide. We emphasize the importance of a careful and systematic search of the electronic ground state in the DFT +U method in order to achieve the true stable state. We propose a method which allows to deal with the now well-established problem of the occurrence of several metastable electronic states in LDA+U.[66] This method consists of searching among all the occupation matrices available (corresponding to the electronic configurations allowed by symmetry) the one that leads to the global minimum of energy. Using this technique we are able, in particular, to recover the expected increase in the equilibrium volume of Pu_2O_3 vs U within LDA+U, while the results of Sun *et al.* follow the opposite trend. We argue that they may have been trapped in metastable electronic states. Indeed, we identify one such metastable state that leads to a DOS and a band-gap value very similar to their results.

In conclusion, we emphasize that this study gives reliable and accurate quantitative structural and electronic properties for Pu_2O_3. The computational scheme proposed in this work could be extended to study more complex materials.

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