Electronic and mechanical properties of ordered (Pu, U)O2 compounds:  
A density functional theory +U study

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A R T I C L E   I N F O

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1. Introduction

Actinide based materials possess interesting physical behaviors due to the existence of 5f electrons and have attracted extensive attentions [1–6]. Especially, actinide oxides are widely concerned because of their dominant roles in nuclear fuel cycle [7,8], among which uranium dioxide (UO2) has been the main fuel component employed in studies of UO2 [22–24] and PuO2 [27–30]. Theoretical (FM) conductor [20] instead of insulator reported by experiment [21]. Several approaches, the LDA/GGA + U [22–24], the hybrid density functional of (Heyd, Scuseria, and Enzerhof) HSE [25], and the self-interaction corrected local spin density (SIC-LSD) [11,26], have been developed to correct these failures in ground-state calculations of actinide oxides. The effective modification of pure DFT by LDA/GGA + U formalisms has been widely employed in studies of UO2 [22,24] and PuO2 [27–30]. Theoretically, the LDA/GGA + U formalisms introduce orbital anisotropy and subsequently increase the number of meta-stable states for actinide oxides [31–34]. As a result, they anticipate that UO2 is 1–k antiferromagnetic (AFM) in its ground state [35], instead of the 3–k magnetic and electric-quadrupole orderings [36–38]. Besides, the LDA/GGA + U formalisms are insufficient to produce a nonmagnetic ground state for PuO2 [20,39] that has been experimentally addressed [40–42]. However, apart from the problem
on magnetic arrangements in their ground states, the obtained insulating features of UO₂ and PuO₂, as well as their structural parameters and electronic structures by using the LDA/GGA + U formalisms accord well with experiments. Even the obtained phonon dispersion curves for PuO₂ in DFT + U studies can be very comparable with experimental measurements [20,43]. Therefore, for estimation of physical properties, the DFT + U method can still be reasonable to large extents.

In this work, we systematically calculate the lattice parameters, electronic and mechanical properties of PuₓU₁₋ₓO₂ compounds by employing the DFT + U schemes due to Dudarev et al. [22–24]. We will always keep in minds that our method has its limitations and be very careful when presenting any conclusive statements. The rest of the paper is organized as follows. In Section 2 the computational method is briefly described. In Section 3 we present our results of the electronic and mechanical properties of PuₓU₁₋ₓO₂ compounds. And finally in Section 4, we close our paper with a summary of our main results.

2. Calculation method

Our total-energy calculations are carried out by employing the plane-wave basis pseudopotential method as implemented in Vienna ab initio simulation package (VASP) [44]. The exchange and correlation effects are described by the DFT within local density approximation (LDA) [45]. The projected augmented wave (PAW) method of Blöchl [46] is employed with the frozen-core/C₂⁹ the Hellmann–Feynman forces on them are less than 0.01 eV/Å. A simple approximation. Electron wave function is expanded in plane waves the spherically averaged screened Coulomb energy and the exchange and correlation effects are described by the DFT within local density formulation by Dudarev et al. [22–24]. In this scheme, the electronic and mechanical properties of PuₓU₁₋ₓO₂ compounds, the SOC is not included.

3. Results and discussion

At room-temperature and zero-pressure conditions, the stoichiometric uranium and plutonium dioxides both crystallize in the CaF₂-like fluorite structure with space group Fm3m (No. 225), in which uranium (plutonium) atoms are supposed to form a face-centered cubic sublattice, and oxygen atoms form a simple cubic sublattice. Using the Hubbard parameters of (U = 4.7 eV, J = 0.7 eV) for plutonium and (U = 4.5 eV, J = 0.5 eV) for uranium, we find that the lattice parameter a₀ is 5.36 Å for PuO₂ and 5.45 Å for UO₂, both of which are in good agreement with previous LDA + U results [27,20,8,11] and experimental results [11,50–52]. However, after taking consider of the AFM order along the z ([001]) direction of the f electrons of Pu (U), there will be small differences between the lattice parameter along the z direction (a₀) and along the x ([100]) and y ([010]) directions (a₀) for PuO₂ and UO₂ [18]. And the space group for PuO₂ and UO₂ will reduce to be P4/mmm (No. 123). Interestingly, the calculated c₀/a₀ ratio for PuO₂ and UO₂ are respectively 1.01 and 0.99.

During geometry optimizations for PuₓU₁₋ₓO₂ compounds, symmetries are also allowed to change. The obtained space group is P4/mmm (No. 123) for all considered PuₓU₁₋ₓO₂ compounds in our calculations. The atomic structures for the PuₓU₁₋ₓO₂ compounds with x = 0.0, 0.25, 0.5, 0.75 and 1.0 are respectively shown in Fig. 1a–e. For Pu₀.₅U₀.₅O₂, we have also tried to put each two ura-
nium atomic layers together and interrupted by two neighboring plutonium layers, with the bicollinear magnetic order that two neighboring uranium layers adopt the same spin component opposite to the spin component of the next two neighboring plutonium layers. The computed total energy for such a structure is 1.01 eV higher than the AFM state of the structure shown in Fig. 1c, and thus it is no longer considered in the following. Total energy calculations reveal that the AFM states are more stable than the FM and nonmagnetic (NM) states for all the considered Pu compounds. We can see that the lattice parameters for both of the two magnetic orders obey the Vegard’s law. We can also see from Fig. 2a that for all the ordered PuO2 compounds, the lattice constant is always larger in the AFM than in the FM states, similar to UO2 and PuO2. The AFM* state in Fig. 2 for Pu0.5U0.5O2 represents the tested bicollinear structure that two neighboring uranium layers are interrupted by two neighboring plutonium layers, which is energetically unfavorable. The computed total energies for all the Pu0.5U1−xO2 compounds are shown in Fig. 2b. In our calculation results, the AFM states for UO2 and PuO2 are 0.36 and 0.45 eV lower in energy than the FM states respectively. We can see from Fig. 2b that the considered Pu0.25U0.75O2, Pu0.5U0.5O2, and Pu0.75U0.25O2 compounds all have lower energies in the AFM states than in FM states.

After exploring the atomic structures for the Pu0.5U1−xO2 compounds, we then analyze the chemical bondings between each atom in them. It has already been revealed that the covalencies are different in actinide dioxides. In comparison with the oxygen 2p electronic states, the actinide 5f electronic states go from higher to lower energies from Th to Es. And in the Pu–Am–Cm region, the actinide 5f and oxygen 2p electronic states overlap [6]. Since the mixing of two orbitals is governed in first-order perturbation theory by the reverse of their energy difference, one can expect stronger covalency in Pu–O bonding than in U–O bonding. In the mixed oxide of Pu0.5U1−xO2 compounds, we can still see this character. Fig. 3 shows the charge density distribution in Pu0.5U0.5O2, with the (a) panel depicting the plane that simultaneously contains uranium, oxygen and plutonium atoms and the (b) panel showing the contour plot of the charge density distribution inside the plane. We can see that the charge density around plutonium, uranium and oxygen ions are all near spherical distribution with slightly deformed toward the direction to their nearest-neighboring atoms and there are clear covalent bridges between plutonium and oxygen, and uranium and oxygen ions. The minimum value of charge density along the Pu–O and U–O bonds are 0.52e/Å3 and 0.48e/Å3 respectively, indicating that the Pu–O bond has stronger covalency than the U–O bond. This result is in good accordance with previous HSE study of the covalencies in Ref. [6]. We have also applied the Bader method [53,54] to analyze the charge transfer in Pu0.5U0.5O2, and the obtained extra charges are −2.45e, −2.63e, and 1.27e for plutonium, uranium, and oxygen atoms respectively. The larger

**Fig. 2.** The lattice parameter $a_0$ (a) and the total energy $E_0$ (b) for different Pu$_{1-x}$U$_x$O$_2$ compounds.

**Fig. 3.** (a) The atomic structure and charge density plane for Pu0.5U0.5O2; (b) Contour plot of the charge density distribution in the charge density plane for Pu0.5U0.5O2. Charge density values are in units of $e$/Å$^3$. 
charge transfer from uranium to oxygen atoms than from plutonium atoms indicates that there is more ionicity in the U–O bond than in the Pu–O bond. In comparison with the charge transfer in PuO₂ and UO₂ [20], the plutonium and uranium atoms in Pu₀.₅U₀.₅O₂ both lose more electrons to oxygen atoms, indicating that the Pu–O and U–O bonds have more ionic characters in the mixed compounds.

The electronic interaction between oxygen and uranium, plutonium atoms is further discussed by calculating the projected density of states (PDOSs). As reported in previous studies [6], the U–O bondings in UO₂ show different covalency from the Pu–O bondings in PuO₂. From the calculated PDOS results for UO₂ shown in Fig. 4a, we can see that the oxygen 2p and uranium 5f electronic states are well separated from each other, and the valence states nearest to the Fermi level are mainly contributed by uranium 5f electronic states. In contrast, the oxygen 2p and plutonium 5f electronic states are found to overlap with each other and the highest valence states are contributed by both the plutonium 5f and oxygen 2p electrons, as shown in Fig. 4c and reported previously in various studies [6,11,27]. The energy band gaps for PuO₂ and UO₂ are found to be 1.67 and 1.53 eV, in good agreement with previous DFT + U studies [20,35] and qualitatively according with the experimental results of 1.8 [21] and 2.1 eV [55]. Our electronic structure result for UO₂ is also consistent with corresponding experimental observations in that the band width of the occupied 5f states near the Fermi energy is 2.0 eV [30,56]. These electronic structure results for UO₂ and PuO₂ prove the effectiveness of our calculation methods.

As a representative for Pu₁₋ₓUₓO₂ compounds, the PDOS for Pu₀.₅U₀.₅O₂ in AFM state is shown in Fig. 4b. Interestingly, we find that in Pu₀.₅U₀.₅O₂, the plutonium and uranium 5f electronic states still keep their localized characters showing very similar distribution shapes with that in PuO₂ and UO₂, and the plutonium and uranium 5f electronic states do not overlap at all. As a result, the electronic structure of Pu₀.₅U₀.₅O₂ can be roughly seen as a superposition of the PuO₂ and UO₂ electronic structures. If the panels are aligned according to the oxygen band edge, it is clear that the occupied uranium 5f states enter above the valence edge of PuO₂ and drastically reduces the gap. A similar discovery has also been made in a recent study on the (Ce, Th)O₂ alloys, where it is found that the cerium 5f orbital lies in the intermediate zone of band gap of ThO₂ [16]. Both of the previous and our present studies indicate that by alloying different actinide dioxides into MOX, we may be able to manipulate the electronic band gaps of the materials. The electronic structures for Pu₀.₅U₀.₅O₂ and Pu₀.₇₅U₀.₂₅O₂ are very similar to what we discover for Pu₀.₅U₀.₅O₂. The three compounds all adopt the spin-down uranium 5f states as the highest occupied states, and the plutonium spin-up 5f states as the lowest unoccupied states. The corresponding energy band gaps for Pu₀.₅U₀.₅O₂, Pu₀.₇₅U₀.₂₅O₂, and Pu₀.₇₅U₀.₂₅O₂ are 0.21, 0.19 and 0.15 eV respectively.

After the systematical electronic structures studies, we now focus on the mechanical properties of Pu₁₋ₓUₓO₂ compounds. The elastic constants for different Pu₁₋ₓUₓO₂ compounds are systematically calculated by using Hooke’s law and perturbation method. A series of small strain ε is firstly applied onto each compound, and then the crystal energies E(ε) which can be expanded as a Taylor series according to Hooke’s law are calculated from first-principles methods. The elastic constants of Pu₁₋ₓUₓO₂ compounds can then be determined from the Taylor expansion expressions of [57]

\[ E(ε) = E(0) + \sum_{ij} C_{ij} \varepsilon_i \varepsilon_j + \frac{1}{2!} \sum_{ijk} C_{ijk} \varepsilon_i \varepsilon_j \varepsilon_k + \cdots \]

where \( E(0) \) is the energy of the unstrained system with the equilibrium volume \( V_0 \). \( \varepsilon \) is the added small strain tensor, and \( C_{ij} \) are the elastic constants. For tetragonal structures, there are six independent elastic constants \( (C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, \text{ and } C_{13}) \). So, the elastic constants for Pu₁₋ₓUₓO₂ compounds can be calculated from six different strain lines as follows:

\[ \varepsilon^1 = (\delta, 0, 0, 0, 0, 0), \quad \varepsilon^2 = (0, 0, \delta, 0, 0, 0), \quad \varepsilon^3 = (0, 0, 0, \delta, 0, 0), \]
\[ \varepsilon^4 = (0, 0, 0, 0, \delta, 0), \quad \varepsilon^5 = (\delta, 0, 0, 0, 0, 0), \quad \varepsilon^6 = (0, \delta, 0, 0, 0, 0). \]

Our calculated elastic constants for PuO₂, UO₂, and Pu₁₋ₓUₓO₂ with the δ value of 0.006 are collected in Table 1. Mechanically, we find that PuO₂, UO₂ and all Pu₁₋ₓUₓO₂ compounds are stable due to the fact that their elastic constants satisfy the following mechanical stability criteria of tetragonal structure [57]:

\[ C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0, \quad (C_{11} - C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{12}) > 0, \quad [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0. \]

In comparison with previous studies, our work seems to be the first one that considers the difference of the AFM aligning direction \( z \) with the \( x, y \) directions, and applies geometry optimizations unisotropically for UO₂. Therefore, there are only three independent elastic constants in previous studies and six in our work. Besides, in order to compare the mechanical properties of PuO₂, UO₂ and Pu₁₋ₓUₓO₂ compounds, we used the same tetragonal lattice for them, which is twice big than the cubic lattice of fluoride PuO₂ or

![Fig. 4. The projected density of states (PDOSs) for the oxygen 2p, plutonium 5f, and uranium 5f electrons in UO₂ (a), Pu₀.₅U₀.₅O₂ (b), and PuO₂ (c). The Fermi energies are set to be zero and denoted by a dotted line. The negative values represent for spin-down electrons.](image-url)
UO₂. Therefore, the elastic constant values are hard to be compared directly with previous reports. However, as we will see later, our calculated bulk modulus for UO₂ based on the tetragonal lattice are close to previous DFT + U results based on the fluorite lattice.

After obtaining elastic constants, we can further calculate bulk and shear moduli from the Voigt–Reuss–Hill (VRH) approximations [58]. The Voigt (Reuss) bounds on the bulk modulus \(B\) and shear modulus \(G\) for the tetragonal crystal structure are deduced from the formulae of elastic moduli [59]. Interestingly, we find that the Voigt and Reuss bounds of bulk modulus are the same for PuO₂, UO₂, and all Pu₁ₓU₁₋ₓO₂ compounds. Nevertheless for shear modulus of them, the Voigt bound is a little different from the Reuss bound, as listed in Table 2. Based on the Hill approximation [58], the bulk and shear moduli can be estimated by \(B = \frac{1}{2}(B₂ + B₃)\) and \(G = \frac{1}{2}(G₂ + G₃)\), and the Poisson's ratio \(\sigma\) can be calculated by:

\[
\sigma = \frac{(3B - 2G)}{2(3B + G)}
\]

The calculated bulk and shear moduli, Voigt and Reuss bounds for the shear modulus, and the Poisson's ratio are summarized in Table 2. Based on the Hill approximation [58], the bulk and shear moduli can be estimated by \(B = \frac{1}{2}(B₂ + B₃)\) and \(G = \frac{1}{2}(G₂ + G₃)\), and the Poisson's ratio \(\sigma\) can be calculated by:

\[
\sigma = \frac{(3B - 2G)}{2(3B + G)}
\]

The calculated bulk and shear moduli, Voigt and Reuss bounds for the shear modulus, and the Poisson's ratio are summarized in Table 2. For PuO₂, UO₂ and Pu₁ₓU₁₋ₓO₂ compounds. From all the data listed in Table 2, we can see that our result of bulk modulus is in better agreement with experiments for UO₂ than for PuO₂. However, we can see from Table 2 that this is a common finding for all theoretical studies. And our calculated bulk modulus for PuO₂ are in good agreement with previous results calculated by the LDA + U [29,20], LDA + U + SOC [39], HSE [29], and SIC-LSD methods [11]. The calculated Poisson's ratio for UO₂ is in agreement with the experimental value of 0.31–0.32 [63–65], while the Poisson's ratio for PuO₂ is in very good agreement with previous theoretical results [59]. Interestingly, we find that the Voigt and Reuss bounds of bulk modulus are the same for PuO₂, UO₂, and all Pu₁ₓU₁₋ₓO₂ compounds. Nevertheless for shear modulus of them, the Voigt bound is a little different from the Reuss bound, as listed in Table 2. Based on the Hill approximation [58], the bulk and shear moduli can be estimated by \(B = \frac{1}{2}(B₂ + B₃)\) and \(G = \frac{1}{2}(G₂ + G₃)\), and the Poisson's ratio \(\sigma\) can be calculated by:

\[
\sigma = \frac{(3B - 2G)}{2(3B + G)}
\]

4. Conclusion

By using the LDA + U method, we have systematically studied the atomic and electronic structures, and mechanical properties of Pu₁ₓU₁₋ₓO₂ compounds with \(x = 0.25, 0.5, \) and 0.75. After full geometry optimizations, we find that all the compounds belong to the P4/mmm (No. 123) space group. Their lattice constants and total energies in both the FM and AFM states obey the linear Vegard's law with different concentrations \(x\). Through careful charge density calculations and analysis, we find that the Pu–O and U–O chemical bondings in Pu₁ₓU₁₋ₓO₂ compounds are still similar to that in PuO₂ and UO₂, but show more ionic characters. Detailed PDOS calculations further reveal that in MOX, the uranium and plutonium 5f electronic states still keep localized characters, similar to that in PuO₂ and UO₂. Besides, the uranium and plutonium 5f electronic states do not overlap with each other, resulting in that the three order Pu₁ₓU₁₋ₓO₂ compounds have much smaller energy band gaps than PuO₂ and UO₂.

The elastic constants and moduli are further calculated for the different Pu₁ₓU₁₋ₓO₂ compounds. It is found that all the Pu₁ₓU₁₋ₓO₂ compounds satisfy the stability criteria for elastic constants of tetragonal structures, and thus are mechanically stable. Our calculated bulk and shear modulus, and Poisson's ratio for PuO₂, UO₂, and Pu₁ₓU₁₋ₓO₂ compounds accord well with previous theoretical results and corresponding experimental measurements. And our results indicate that the mechanical properties of all the Pu₁ₓU₁₋ₓO₂ compounds are similar to that of PuO₂ and UO₂.

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Table 2

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<th>Compound</th>
<th>Reference</th>
<th>(B)</th>
<th>(G)</th>
<th>(G_Y)</th>
<th>(G_X)</th>
<th>(\sigma)</th>
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<td>PuO₂</td>
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<td>95</td>
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<td>109</td>
<td>115</td>
<td>0.27</td>
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<tr>
<td>Pu₀.₅U₀.₅O₂</td>
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<td>219</td>
<td>107</td>
<td>106</td>
<td>108</td>
<td>0.29</td>
</tr>
<tr>
<td>Pu₀.₂₅U₀.₇₅O₂</td>
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<td>117</td>
<td>111</td>
<td>123</td>
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<td>–</td>
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<tr>
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References
