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LDA+U Study on Plutonium Dioxide with Spin-Orbit Couplings

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We perform first-principles density functional calculations on plutonium dioxides considering proper relativistic effects and strong correlations with the LDA+U method. Though this material is a paramagnetic insulator, standard local density approximation (LDA) predicts metallic states. In this paper, we point out that not only strong correlations but also spin-orbit couplings as relativistic effects are necessary to obtain paramagnetic insulating states. Based on this proper method, we also calculate physical properties of plutonium dioxide and compare them with experiments.

KEYWORDS: plutonium dioxide, nuclear fuel, first-principles calculation, LDA+U, spin-orbit coupling, elastic constants

I. Introduction

Plutonium dioxide (PuO_2) is a main compound of a mixed oxide (MOX) fuel, and its physical properties are important in the nuclear fuel developments. However, the experimental data has still remained insufficient because of severe difficulties on its experimental treatments. Then, calculations without any limitation play an important role.

The first-principles density functional theory (DFT) has been expected to obtain the physical properties of PuO_2 without any empirical parameters. However, the standard DFT with local density approximation (LDA) predicts a metallic ground-state, which is inconsistent with the insulating state observed in experiments. Though this disagreement can be due to strong correlation of Pu f-orbital electrons, even modern correction schemes such as LDA+U[1] and hybrid DFT[2] taking account of strong correlation effects on f-orbital electrons are known to fail to reach the paramagnetic insulating ground state. Indeed, these schemes can give insulating states but always generate unexpected ferromagnetic or antiferromagnetic order together.[3] To our knowledge, only a few literatures considering the spin-orbit coupling in addition to the correlation effects (SIC-LDA,[4] LDA+DMFT,[5] and a specific LDA+U[6]) successfully obtained the paramagnetic insulating state. In this paper, we evaluate the electronic states using LDA+U with spin-orbit coupling, and reach the paramagnetic insulating state of PuO_2 in calculations. Besides, we calculate several physical properties using the obtained paramagnetic insulating state.

This paper is organized as follows. The calculation methods are explained in Section II, and the fundamental properties of PuO_2 are described in Section III. The calculated results are shown in Section IV, and Section V gives conclusions.
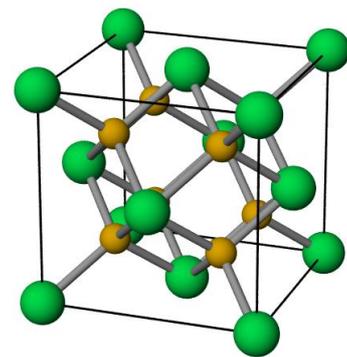

Fig. 1 The crystal structure of PuO_2. The large and small spheres stand for Pu and O atoms, respectively. Black cube denotes the unit cell.

II. Method

We calculate the properties of PuO_2 with the first-principles density functional theory. The package we employ through this paper is VASP,[7] which adopts the PAW method[8] with LDA[9] exchange-correlation energy. In addition, VASP supports LDA+U method[1] for strongly-correlated systems and spin-orbit coupling as a relativistic effect. Through this paper expect for oxygen-deficiency calculation, we fix the parameters $U = 4$ eV and $J = 0$ eV for LDA+U. These values have been confirmed by comparing the calculated lattice constants and gap-size with those observed in experiments.[10] At the end of this section, we summarize the parameters used in the density functional calculations. k-points are set to $9 \times 9 \times 9$ and self-consistent loops are repeated until the energy difference becomes less than 10^{-7} eV, with cut-off energy 500 eV.

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III. Material

The crystal structure of PuO$_2$ is the same as fluorite (CaF$_2$) as shown in **Fig. 1**. This structure has cubic symmetry, and its space group is $Fm\bar{3}m$. Pu atoms form an fcc cell, and O atoms occupy six sites at $(\pm0.25, \pm0.25, \pm0.25)$ in internal coordinates. The lattice constant, which corresponds to the length of the edge of the unit cell in Fig. 1, is 5.396 Å.[11]

As for the materials properties, PuO$_2$ is known to be an insulator, same as other actinide dioxides, such as UO$_2$. In addition, PuO$_2$ does not have any order even at low temperature, while UO$_2$ and NpO$_2$ have 3-q antiferromagnetic[12] and multipole orders,[13] respectively.

IV. Calculated Results

1. Insulating State

As mentioned in Section III, PuO$_2$ is known to be a paramagnetic insulator. However, standard DFT calculations predict metallic states. This failure is because of lack of strong correlation and spin-orbit coupling (SOC). In the $5f$-orbital electron system, such as actinides, it is known that the electronic correlation becomes too strong to calculate correct electronic states with LDA. Besides, the spin-orbit coupling as a relativistic effect cannot be neglected any longer in actinide systems. Therefore, we adopt LDA+U method including the strong-correlation effect, and the spin-orbit coupling is also involved. We obtain the paramagnetic insulating state by considering these effects.

Figure 2 shows the calculated band structure and density of states(DOS). The results calculated by standard LDA are displayed in Fig. 2(a). In this figure, f-orbitals exist around the Fermi energy. However, no gap opens, and therefore the obtained electronic state is not insulating. On the other hand, a gap, whose size is around 2 eV, opens in Fig. 2(b), where the results are obtained by LDA+U ($U = 4$ eV) with SOC. This gap size agrees with the experimental data.[14] As shown in DOS, f-orbitals split into occupied and unoccupied states, and occupied states are hybridized with O p-orbitals.

The reason why the paramagnetic insulating state is obtained by LDA+U with SOC can be explained in the following way. Pu^{4+} cation has 4 electrons in its f-orbitals. When applying the spin-orbit coupling, the f-orbitals split into $j = 5/2(= 3 - 1/2)$ and $j = 7/2(= 3 + 1/2)$ states, where j is the total angular momentum. The six-fold $j = 5/2$ states have lower energy than $j = 7/2$ ones, and therefore all 4 electrons are involved in the six-fold $j = 5/2$ states. According to crystal field theory, $j = 5/2$ states separate into Γ_7 doublet and Γ_8 quartet in the cubic symmetry. The four electrons in Pu f-orbitals fully occupy the Γ_8 quartet, and strong correlation described by the Hubbard U opens a gap between occupied Γ_8 and unoccupied Γ_7. This argument is confirmed by the results shown in **Fig. 3**. Thus, the paramagnetic insulating state is formed due to both of the strong correlation and SOC. When SOC is neglected, f-orbital states has no fourfold state and it is impossible to achieve a paramagnetic insulating state. Moreover, the strong correlation is necessary to open an insulating gap.

Table 1 shows differences between total energies with and without SOC for $U = 0$ and 4 eV. In both cases, the differ-
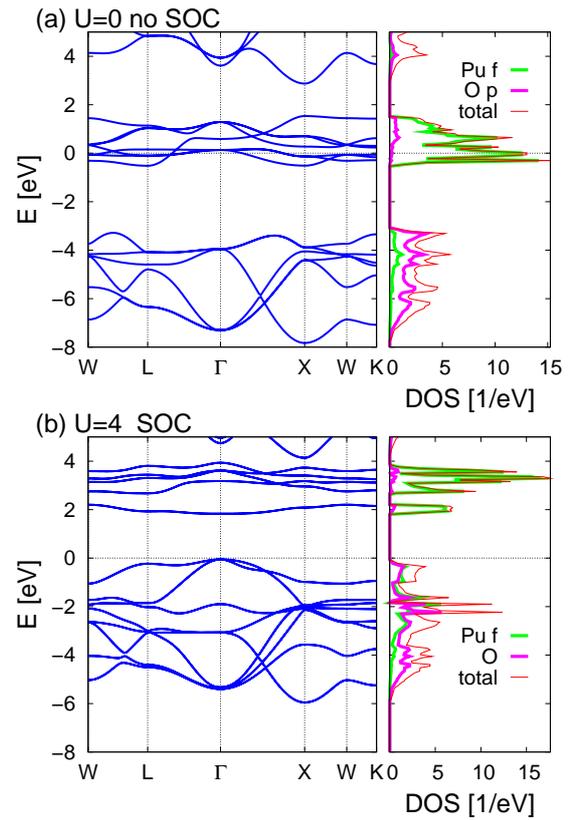

Fig. 2 Band structure and density of states for PuO$_2$ obtained by standard LDA without SOC (a) and by LDA+U ($U = 4$eV) with SOC. The Fermi energy is set to zero.
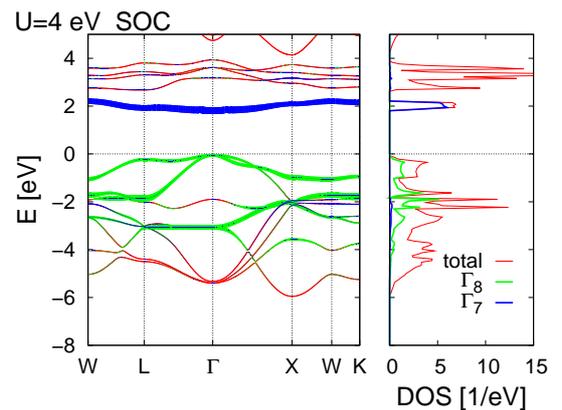

Fig. 3 Band structure and projected density of states for Γ_7 and Γ_8 states in Pu f-orbitals. The thickness of green (blue) curves in the left panel denotes the contribution of Γ_8 (Γ_7) states. The calculations are done by LDA+U ($U = 4$ eV) with SOC.

Table 1 Energy difference, ΔE, between spin-orbit and no-spin-orbit calculations. ΔE is defined as $E_{\text{SOC}} - E_{\text{NO-SOC}}$, where E_{SOC} and $E_{\text{NO-SOC}}$ are total energies per formula unit(PuO$_2$) with and without spin-orbit couplings, respectively. U is the parameter of LDA+U.

U (eV)	ΔE (eV)
0	-4.54
4	-8.93

Table 2 Calculated elastic constants of PuO$_2$ with LDA+U ($U = 4$ eV) with SOC.

c_{11} (GPa)	c_{12} (GPa)	c_{44} (GPa)
412	141	72

ences are large and not negligible, and SOC makes the total energies smaller. In particular, the energy difference for $U = 4$ eV are larger than that of $U = 0$. This large difference may be caused by the insulating state obtained only for the combination of LDA+U and SOC. Thus SOC intensely affects also the total energy.

In order to confirm whether this paramagnetic insulating state is the ground state, we compare the total energy of ferromagnetic state with that of the paramagnetic one. As a result, the total energy of the paramagnetic state is larger than that of the ferromagnetic. This indicates that the obtained paramagnetic state is not the ground state. Though this state is metastable in the calculation, it exhibits the important properties, such as an insulating gap and non-magnetic order. We believe that this paramagnetic state is better to evaluate various physical properties than any other state obtained by DFT calculations so far.

2. Elastic Constants

Based on the paramagnetic insulating state obtained in the previous section, we also calculate mechanical properties. First, we have to find an optimized structure in first-principles calculations. Using LDA+U ($U = 4$ eV) with SOC, we optimize the lattice constant and find that total energy is minimized with a lattice constant 5.35556 Å. This value is almost consistent with experimental value 5.367 Å. Note that the calculated lattice constant corresponds to that at zero temperature, while the experimental value is observed at room temperature. When considering thermal expansion, the observed value can be slightly larger than the calculated one. In many cases, GGA is more suitable than LDA, for calculations of atomic forces and stress tensors. However, in this case, GGA+U with $U = 4$ eV overestimates the lattice constant (5.460 Å). This results implies that GGA+U is inadequate for the stress calculations, and we adopts LDA+U method for this material.

Elastic constants are evaluated from the stress tensors on the strained structure.[16] We set the strength of the strain to 1.5 %. The results are summarized in **Table 2**. Due to cu-

Table 3 Mechanical properties of PuO$_2$.

	Bulk modulus B (GPa)	Shear modulus G (GPa)	Young modulus Y (GPa)	Poisson's ratio σ
Voigt	232	98	257	0.315
Reuss	232	89	237	0.330
Hall	232	93	247	0.322
Exp.	178[17]	—	268.4[18]	0.28[18]

bic symmetry, there are only three independent constants, c_{11}, c_{12}, and c_{44}. Bulk modulus B, shear modulus G, Young modulus Y and Poisson's ratio σ are also estimated by using these elastic constants.[15] Three approximations to calculate these moduli through elastic constants are known. In the Voigt approximation, bulk and shear moduli are defined by

$$B_{\text{Voigt}} = \frac{1}{3}\left(c_{11} + 2c_{12}\right) \tag{1}$$

$$G_{\text{Voigt}} = \frac{1}{5}\left(c_{11} - c_{12} + 3c_{44}\right). \tag{2}$$

On the other hand, these moduli in the Reuss approximation are expressed as

$$B_{\text{Reuss}} = \frac{1}{(3s_{11} + 6s_{12})} \tag{3}$$

$$G_{\text{Reuss}} = \frac{5}{(4s_{11} - 4s_{12} + 3s_{44})}, \tag{4}$$

where stiffness constants s_{11}, s_{12}, and s_{44} are defined as

$$s_{11} = \frac{c_{11} + c_{12}}{c_{11}^2 + c_{11}c_{12} - 2c_{12}^2} \tag{5}$$

$$s_{12} = -\frac{c_{12}}{c_{11}^2 + c_{11}c_{12} - 2c_{12}^2} \tag{6}$$

$$s_{44} = \frac{1}{c_{44}}. \tag{7}$$

The third is the Hall approximation, where moduli are obtained as the average of the Voigt and the Reuss approximations, e.g., $B_{\text{Hall}} = (B_{\text{Voigt}} + B_{\text{Reuss}})/2$. The Young modulus Y and Poisson's ratio σ are determined by the bulk modulus B and shear modulus G,

$$Y = \frac{9BG}{G + 3B} \tag{8}$$

$$\sigma = \frac{1}{2}\frac{3B - 2G}{3B + G}. \tag{9}$$

It is known that the Voigt approximation gives the maximum of the moduli, while the Reuss one gives the minimum. The calculated moduli are shown in **Table 3**. Though there are few papers about the observed elastic constants and related values, the bulk modulus, Young modulus, Poisson's ratio have been reported as 178 GPa,[17] 268.4 GPa, and 0.28,[18] respectively. The calculated values are almost in good agreement with these data, but more sophisticated methods might be necessary to obtain more accurate agreements.
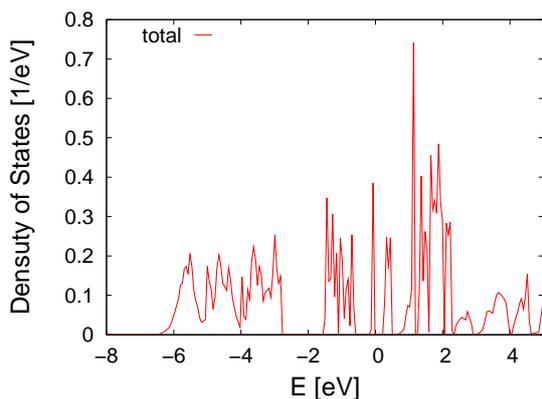
Fig. 4 Density of states of Pu_4O_7.

3. Oxygen Deficiency

For the nuclear fuel, sub-stoichiometric plutonium dioxides PuO_{2-x} are used to reduce oxygen gas after burning. We also evaluate the effect of the oxygen defect on the electronic structure. In order to investigate the oxygen defect, we use the hypothetical material Pu_4O_7 ($PuO_{1.75}$), which is formed by removing an O atom from the unit cell shown in Fig. 1. Though this material is not realistic, it is the most simple model containing the oxygen defect. **Figure 4** indicates the density of states of Pu_4O_7. This result is calculated with LDA+U ($U = 2$ eV) with SOC. Comparing it with the DOS of stoichiometric PuO_2, there is a sharp peak just below the Fermi energy. This peak corresponds to Γ_7 doublet, which is empty in the case of PuO_2. Removing an O^{2-} anion corresponds to doping 2 electrons, and then the doped electrons occupy the Γ_7 states. Note that even number of doping electrons can keep a paramagnetic state. Thus, oxygen deficiency makes the gap shrink, but still leaves paramagnetic.

V. Conclusion

We obtained a paramagnetic insulating state of PuO_2 by first-principles LDA+U method with the spin-orbit coupling. In the present calculation, the spin-orbit coupling plays an important role in addition to the strong correlation effect through LDA+U. Mechanical properties were also evaluated using the paramagnetic state. Moreover, we investigated how oxygen deficiency affects the electronic state and found that the deficiency keeps the electronic state paramagnetic.

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