First Principle Studies on Electronic and Defect Structures of UO$_2$, ThO$_2$, and PuO$_2$

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1. Introduction

Many studies have been undertaken regarding light actinide dioxides (AnO$_2$), not only because of their technological interest but also because of their peculiar fundamental properties, which are often linked with their 5f electrons. Light AnO$_2$ exhibits multiple oxidation states and, as a subgroup, displays a greater chemical variety than "heavy" actinides from curium through to lawrencium. The purpose of this study is to obtain an improved electronic structure of three light AnO$_2$, which are ThO$_2$, UO$_2$, and PuO$_2$. We calculate the total and local electronic density of states and the electronic energy band structure of the three oxides, by using the spin polarized generalized gradient approximation(SP-GGA)+U and projector-augmented wave (PAW) method based on the DFT method. Further, we calculate the intrinsic defect formation energies to understand the effect of a partially filled 5f band on a defect generation in the three AnO$_2$. For the calculations of the defect formation energies, the PAW-GGA method is employed. The U parameter is considered only when calculating an electronic structure of the three oxides. We assume that the effect of U is very small when a defect formation energy is calculated from the energy difference between the two systems, because the total energy of the system is proportional to the U parameter. To reduce the artificial error due to the use of a small supercell for the calculation of a defect formation energy, we use a large supercell containing 96 atoms.

2. Methods and Results

2.1 Calculation details

For the electronic structure of a perfect crystal of the three oxides, the SP-GGA+U calculations were performed by using the Perdew-Wang 91 exchange-correlation functional [1] and a plane-wave basis as implemented in the VASP code [2,3]. To describe the electron-ion interaction, the PAW potential was employed [4], and a cut-off energy of 400 eV was used to expand the wave functions. The charge density was obtained by using a $6 \times 6 \times 4$ k-point grid within the Brillouin zone (BZ). In this work, we used a simplified Dudarev's scheme to include the Coulomb correlation U [5], which is an invariant form with respect to a unitary transformation of the L(S)DA+U functional proposed by Anisimov *et al* [6].

There are two types of intrinsic defects commonly observed in AnO$_2$: Anion Frenkel and Schottky trio defects. We calculated the formation energies of these two intrinsic defects by using a $2 \times 2 \times 2$ supercell containing 96 atoms. An anion Frenkel defect is a pairing of a vacancy and an interstitial of an oxygen atom. The formation energy of an anion Frenkel pair, E_{FP}^{f}, is given by,

$$E_{FP}^{f} = E_{V_O}^{N-1} + E_{I_O}^{N+1} - 2 \times E^{N} \qquad (1)$$

where E^{N} is the total energy of a perfect crystal containing N atoms. $E_{V_O}^{N-1}$ is the total energy of a system with an oxygen vacancy (V$_O$). To calculate the total energy of $E_{I_O}^{N+1}$, we inserted an oxygen-excess atom (I$_O$) into an octahedral interstitial site in an FCC structure. We calculated the Schottky defect formation energy in the three oxides by using Eq. (2).

$$E_{SD}^{f} = E_{V_{An}}^{N-1} + 2 \times E_{V_O}^{N-1} - 3 \times E^{N} - \mu_{AnO_2} \qquad (2)$$

where μ_{AnO_2} is the chemical potential of three atoms corresponding to a Schottky defect, which is one actinide and two oxygen atoms. In this study, we used the cohesive energy of a unit cell as the chemical potential of the three defect atoms. To describe the electron-ion interaction, the PAW potential was employed [4] and the GGA method was used to calculate the exchange-correlation energy of the electrons. The charge density was obtained by using a $2 \times 2 \times 2$ k-point sampling over the BZ. For each defect structure, an ionic relaxation was carried out until the force per atom became smaller than 0.01 eV/Å. All the energy calculations were performed by using the VASP code [2,3].

2.2 Results and Discussion

ThO$_2$ has a non-magnetic ground state, but we calculated with the magnetic moments of 1.81 and 3.97 μ_B for UO$_2$ and PuO$_2$, respectively, with an antiferromagnetic ordering along the [001] direction. We calculated the local electron density of states (LDOS) of UO$_2$ and PuO$_2$ and found that the magnetic property is caused by the partially occupied U and Pu 5f bands as shown in Fig. 1. The spin-down components of the U and Pu 5f states are almost completely unoccupied and thus a non-zero magnetic moment is developed at each U and Pu ion. We checked the magnetization of 6d for the U and Pu atoms, and obtained a very small value of about 0.02 μB. These results confirm that the magnetic structures of UO$_2$ and PuO$_2$ are governed by

the partially filled U and Pu $5f$ bands. This result agrees well with experimental information that the magnetic properties of actinide oxides are clearly related to the magnetic moment of the $5f$ electrons which are considered to be localized in the actinide ions [7].
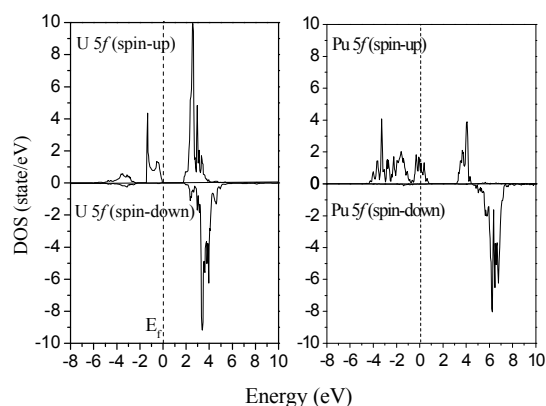

Figure 1. Spin-decomposed local density of states for U and Pu $5f$ orbitals. The difference in the spin-up and spin-down DOS leads to the antiferromganetic ordering of UO_2 and PuO_2.

Next, we calculated the intrinsic defect formation energies of the three oxides. A defect is an important factor to understand the diffusion and transport processes in materials. Table 1 shows the calculated formation energies for the two dominant intrinsic defects of the three AnO_2. The energy values of UO_2 and PuO_2 agree with other theoretical and experimental results in that the Frenkel pair formation energy is in the range of 4~5 eV and the Schottky trio energies are 8~10 eV [8]. Especially, the present energy values of UO_2 are in excellent agreement with the experimental data of 3.0-4.6 and 6.0-7.0 eV, respectively.

Table 1 Calculated formation energies of the oxygen Frenkel pair and Schottky trio defects in light AnO_2.

(eV)	ThO_2	UO_2	PuO_2
Oxygen Frenkel pair	9.81	3.68	4.42
Schottky defect	20.56	6.95	7.11

We suggest that the much larger formation energies for ThO_2 have a relevance to it's stable stoichiometric property. The deviations from an exact stoichiometry are accompanied by the formation of a Frenkel defect on the oxygen-ion sublattice of a crystal [9]. To ensure the electrical neutrality in a crystal when oxygen ions are removed from or added to an exactly stoichiometric material requires that some of the cations change their valence. Therefore, uranium and plutonium ions have many valence states such as 3+, 5+, and 6+ in UO_2 and PuO_2. However ThO_2 is known to be a highly stable stoichiometric oxide, and the valence of a thorium ion is unlikely to change from 4+. This difference can be explained from the absence of $5f$ electrons in ThO_2. The

stoichiometry deviation of UO_2 and PuO_2 is allowed by the presence of partially filled $5f$ shell. There are three and six electrons in $5f$ shell of free uranium and plutonium atoms. As a result, a defect is hardly created in ThO_2 more than in UO_2 and PuO_2.

3. Summary

We investigated the electronic structure of the three AnO_2. We found that the magnetic moment was governed by the almost complete spin-polarization of the partially filled the $5f$ band as well except ThO_2 which has non-magnetic ground states. We calculated the formation energies of two intrinsic defects in the AnO_2 and suggested that the lower defect formation energies in UO_2 and PuO_2 than in ThO_2 are related to their various oxidization states, because the partially filled $5f$ states play an active role in accommodating an oxygen vacancy or interstitial by transferring electrons between the actinide ion and the oxygen vacancy or interstitial. Our calculations demonstrate that the $5f$ electrons should be taken into account for a reliable description of the physicochemical properties of actinide oxides.

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