First-principle study of physical/chemical properties of uranium oxides

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1. Introduction

Physical and chemical properties of uranium oxides should be well understood for efficient energy generation and long-term storage of high-level radioactive wastes. Extensive research on this field, however, may consume a lot of time and resources. In this research, a first-principle calculation based on the density functional theory (DFT) was employed to obtain various physical properties of uranium oxides. The band gap, bulk modulus, lattice constants, and magnetic moment of UO_2 have been studied. Also the oxidation/reduction energies for uranium oxides have been calculated.

2. Methods and Results

DFT is the most conventional approach to investigate many solid-state materials theoretically. However, DFT shows the limitation in describing *d*- and *f*-block elements and their compounds due to the electron correlation effect of *d*- or *f*-electrons. In this research, we performed the local-spin-density approximation (LSDA) and the LSDA combined with the Coulomb interaction *U* (LSDA+*U*) for the calculation of uranium oxides. *U* is included to describe correlation effect of uranium 5*f*-electrons. For the calculations, the full-potential augmented plane wave plus local orbital method has been used with WIEN2k package [1].
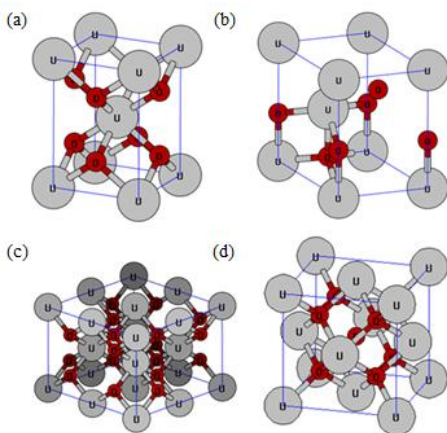
2.1 Crystal structures of uranium oxides

AO_2, A_2O_3, and A_4O_9 (A = actinide elements) are general species in the actinide oxides. First, various physical properties of UO_2 have been calculated and compared to the experimental results. Then, the total energies of U_2O_3 and U_4O_9 are calculated for testing the oxidation and reduction energies of uranium oxides. The crystal structures of each uranium oxides are shown in Fig. 1.

Crystal structure of UO_2 is well known from experiments, and those are used here. Because other oxides are not well studied, we have constructed them based on other actinide oxides. U_4O_9 is constructed by adding an extra oxygen atom into the center of the UO_2 unit cell [2]. Bulk U_2O_3 is nonexistent in nature, so the crystal structure of Pu_2O_3 is used to construct that of U_2O_3 [2, 3, 4, 5]. Pu_2O_3 at the room temperature has a complicated structure, so we have constructed a simpler one keeping the stoichiometry and local structures [2, 5].

2.2 Electronic structures of UO_2 from LSDA and LSDA+*U* method

Figure 2 shows the electronic density of states (DOS) obtained by the LSDA and LSDA+*U* method. The LSDA presented the metallic ground state of UO_2, which is not consistent with the insulating ground state observed in experiments. This means that the naïve LSDA method is insufficient to describe the correlation effect of U 5*f*-electrons. The LSDA+*U* method, however, presented clear band gap near the Fermi level indicating the insulating ground state of UO_2.

Fig. 1. (a) Crystal structures of UO_2 (b), β-U_2O_3 (c), α-U_2O_3 (d), and U_4O_9. Gray and red spheres indicate the uranium and oxygen atoms, respectively.
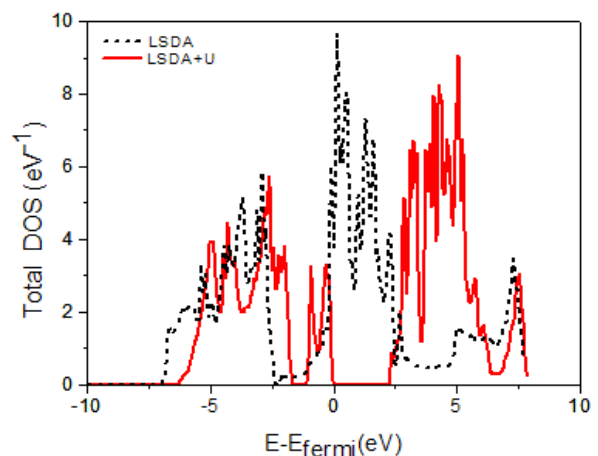

Fig. 2. Electronic density of states for UO_2 from LSDA (black dotted line) and LSDA+*U* (red solid line).

Table I: The calculated properties of UO_2 and comparison with experimental data and other references.

	Experiment[a]	S.L. Dudarev[b]	Yun *et. al.*[15]	This work
Lattice constant (Å)	5.46	5.37	5.44	5.47
Bulk modulus (Gpa)	207	202	209	214
Band gap energy (eV)	2.0	2.1	1.8	2.1
Magnetic moment (μ_B)	1.74	2.1	1.8	1.82

[a] Ref. 6, 7, 8, 9, 10, 11.   [b] Ref. 12, 13, 14.

2.3 Calculated properties of UO_2 from LSDA+U approach

The LSDA+U method correctly describes the correlation effect of uranium 5f-electrons as shown in Fig. 2. The value of U was optimized by adjusting the calculated band gap to the experimental value. When U was set to 4.5 eV, the calculated band gap agreed well with the experimental value. Also, the ground state lattice constants of UO_2 were obtained from the lattice relaxation with the optimization of the volume. Other structural properties of UO_2 were also calculated with same U. The calculated values are verified by comparing with the experimental data[a] and previous calculated results [12,13,14,15]. Our calculation reproduces well the experimental results as shown in Table I.

2.4 Size effect of U on the properties of UO_2

The changes of the band gap energy and the ground state lattice constants with varying U are also studied. The band gap and lattice constants increased with increasing U. The change of band gap is very sensitive to the change of U, but the change of the lattice constants is relatively small.

2.5 Oxidation and reduction energies of UO_2

Oxidation and reduction are influenced by thermodynamic conditions including temperature, pressure and chemical potential of O_2. In this study, however, we assume the absolute zero temperature to remove the entropy contribution in the free energy. Thus, oxidation/reduction energies could be obtained by the following formulae

$$E^{ox} = \frac{1}{4}E(U_4O_9) - E(UO_2) - \frac{1}{8}E(O_2) \qquad (1)$$
$$E^{red} = \frac{1}{2}E(U_2O_3) - \frac{1}{4}E(O_2) - E(UO_2). \qquad (2)$$

$E(A)$ means the total energy of compound A. U was fixed at 4.5 eV in every calculations. The calculated oxidation energy was -0.252 eV/f.u. which is reasonable considering that experimentally UO_{2+x} can be oxidized up to $x = 0.25$, U_4O_9. The reduction energies were 4.885 eV/f.u and 6.325 eV/f.u when UO_2 was reduced to α-U_2O_3 and β-U_2O_3, respectively. The reduction energies

were positive values, which mean that UO_2 is more stable than U_2O_3. The results seem to be reasonable because the bulk U_2O_3 does not exist in nature.

3. Conclusions

In this research, physical and chemical properties of uranium oxides are studied using LSDA and LSDA+U method. The LSDA method fails to predict the ground state for UO_2. The LSDA+U method which considers electron-electron repulsion, however, properly describes the properties of UO_2. The calculated properties including ground state lattice constants, band gap, and magnetic moment agree well with the experimental data. The oxidation and reduction energies of UO_2 also qualitatively describe the natural phenomena. Through this study, we show that LSDA+U can be employed to predict physical/chemical properties of uranium oxides.

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