Density Functional Theory Study of UO$_2$

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1. Introduction

Uranium dioxide (UO$_2$) is an important fuel material for nuclear industry, but the electronic structure of 5f electrons of uranium has not been reliably described so far. The interpretation of some of experimental results is still controversial because of a large variety of unusual electronic effects originating from strong Coulomb repulsion between 5f electrons of uranium. During irradiation, UO$_2$ undergo nuclear fission and the noble gas Xe is formed. Xe diffuses into the gap between the cladding and pellets of the fuel, and causes swelling of the fuel. Point defects are thought to be the major channel of Xe diffusion in UO$_2$ [i, ii]. Therefore, it is important to investigate defects in order to understand the diffusion mechanism in nuclear reactor. We present the density functional theory (DFT) calculations on UO$_2$ employing the local spin density approximation (LSDA) + U method. First, we calculated the chemical and physical properties of bulk UO$_2$ such as the lattice constant, bulk modulus, cohesive energy, magnetic moment, and band gap. We compared the calculated results with available experimented data. Then we performed supercell calculations to investigate the structure of different defects in UO$_2$, the defect formation energy, and the defect-induced changes in the electronic structure.

2.Theory and methodology

In recent years, DFT calculations have made a profound impact on the investigation of material properties. In addition, improvements in computer performance allow to apply these methods to an increasing number of physical and chemical phenomena. Most of DFT calculations are based on the local density approximation (LDA) of the exchange-correlation [iii, iv]. However the LDA calculations often fail to describe systems with strongly correlated 5f electrons, predicting metallic behaviour contrary to the observed insulating behaviour [v]. Orbital-dependent functionals like the LSDA+U approach are known to correct this problem by adding on-site Coulomb repulsion ($\overline{U}$). The 5f Coulomb correlation energy $\overline{U}$ was determined to be 4.6±0.8eV from the energy difference in the two spectroscopy experiments (x-ray photoemission and Bremsstrahlung isochromat spectroscopy) [vi]. We used the parameters of $\overline{U}$ = 4.5eV and $\overline{J}$ = 0.5 from Dudarev *et al.* [vii].

3. Results and discussion

Table. 1. shows the calculated chemical and physical properties of UO$_2$. The calculated equilibrium lattice constant of UO$_2$ is found to be 5.44 Å. It is underestimated by about 0.55 % compared with the experimental value of 5.47 Å [viii]. The cohesive energy per UO$_2$ molecule is calculated to be 26.9 eV, that is larger than the experimental value of 22.3 eV by about 20 %. The underestimation of lattice constant and the overestimation of cohesive energy are typical of DFT-LDA calculations [ix]. The LSDA+U calculations predict the correct insulating ground states, which shows antiferromagnetic ordering, with the band gap of 1.9 eV. In contrast, calculations employing original LDA scheme result in metallic electronic structure with the partially occupied uranium 5f bands.

Table. 1 Cohesive properties of UO$_2$

	Exp.	S.L. Dudarev (LSDA)	S.L.Dudarev (LMTO-ASA)	This work (LSDA+U)
Lattice constant (Å)	5.46	5.27	5.37	5.44
Cohesive energy (eV/ UO$_2$)	22.31	18.63	22.23	26.90*
Bulk modulus (GPa)	207	252	202	209
Magnetic moment (μ_B)	1.74	–	1.7	1.9
Band gap. (eV)	2.0	–	1.3	1.9

* We did not include spin-polarization energy of atoms. Thus our calculated cohesive energy is somewhat overestimated.

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