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First-principles study of thermophysical properties of uranium dioxide

Zhi-Gang Mei [a,*], Marius Stan [a], Jiong Yang [b]

[a] Nuclear Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States
[b] Materials Science and Engineering Department, University of Washington, Seattle, WA 98195, United States

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ABSTRACT

The structural and elastic properties, lattice dynamics and thermophysical properties of uranium dioxide (UO_2) were studied by DFT based first-principles calculations. LDA+*U* method shows the overall best description of the lattice parameters and elastic constants of UO_2 among all the DFT methods studied. The phonon dispersion relations of UO_2 predicted by direct method agree with experimental results. Thermodynamic properties, including Gibbs energy, enthalpy, entropy and heat capacity, were evaluated under quasiharmonic approximation using the calculated phonon density of states. Good agreement with experiments is obtained up to 1000 K. Further improvement of heat capacity at high temperatures can be achieved by taking into account of thermal expansion. The calculated lattice thermal conductivity of UO_2 shows that phonon scatterings by defects are critical at room temperature while three-phonon interactions dominate the phonon scattering at high temperatures.

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1. Introduction

Uranium dioxide (UO_2) is the most widely used fuel for the current nuclear power generation because of its high melting temperature and stable fluorite structure under high dose irradiation. In addition to its technological importance, UO_2 is of great scientific interest as a strongly correlated system. The effect of 5*f* electrons on the bonding and lattice vibration in actinide oxides has attracted considerable attention. To understand the behavior of nuclear fuels in reactors and evaluate the fuel performance during the fuel cycle, it is very important to investigate the fundamental thermophysical properties, such as heat capacity, thermal expansion, and thermal conductivity [1–5]. During the past decades UO_2 has been extensively studied using different experimental techniques [6–9]. Due to the radioactive nature of nuclear fuels and the high cost of related experimental work, computer modeling and simulation have become critical for nuclear fuels studies. With the development of density-functional theory (DFT) methods, it is now possible to calculate the static structural energy of materials in any given structure. Although DFT has been quite successful for light actinide metals [10], standard DFT calculations are less accurate in describing actinide oxides. For example, standard DFT calculations using local density approximation (LDA) or generalized gradient approximation (GGA) predict a ferromagnetic (FM) structure as the ground state of UO_2 instead of the experimentally observed antiferromagnetic (AFM) phase [11]. To overcome the limitation, several advanced DFT techniques have been proposed to better treat the correlated 5*f* electrons. Among these new methods, DFT+*U* is one of the most popular approaches for studying actinide compounds due to its computational efficiency.

The lattice dynamics and thermophysical properties of UO_2 have been studied by several authors using different DFT methods. Yin and Savrasov [12] reported the phonon spectra and thermal conductivity of UO_2 using a combination of a DFT-based technique and a many-body approach. Recently, Sanati et al. [13] investigated the phonon and thermal properties of UO_2 using DFT and DFT+*U* methods. However, the predicted heat capacity was underestimated due to the neglect of thermal expansion. Yun et al. [14] also studied the phonon spectra and heat capacity of UO_2 using standard DFT calculations. Very recently, Pang et al. [15] revisited the phonon dispersion of UO_2 using inelastic neutron scattering and DFT+*U* simulations. Unfortunately, DFT+*U* calculations of UO_2 are known to converge to metastable states that correspond to different uranium 5*f* orbital occupations [16]. Very few studies of UO_2 by DFT+*U* took into account of this issue. Thus further investigation of the thermophysical properties of UO_2 is still important, especially to overcome the shortcomings of the previous studies. Additionally, most of theoretical studies were focused on heat capacity, and there is no systematic study of the thermodynamic properties of UO_2 by DFT+*U* method yet.

In this study we aim at providing a first-principles evaluation of the thermophysical properties of UO_2 using both DFT and DFT+*U* methods. The orbital occupation matrix of 5*f* electrons is properly

* Corresponding author. Tel.: +1 6302522318.
E-mail address: zmei@anl.gov (Z.-G. Mei).

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controlled to ensure that true ground state is reached. The targeted thermophysical properties include Gibbs energy, enthalpy, entropy, heat capacity and thermal conductivity. By studying Gibbs energy and heat capacity, we provide fundamental information for the thermodynamic modeling of higher-order oxide systems, such as mixed oxide fuels. The rest of the paper is organized as follows: Section 2 provides the details for the calculations of total energy and phonon dispersions. Section 3 contains the results and a discussion of the lattice parameters, elastic constants, lattice dynamic, thermodynamic properties and thermal conductivity of UO_2. A summary is given in Section 4.

2. Computational details

The DFT calculations were performed by the projector augmented wave method as implemented in VASP [17,18], within LDA and GGA parameterized by Perdew et al. [19]. The strong correlation between the 5*f* electrons of uranium was described by DFT+*U* method using the Dudarev et al.'s implementation [11], which depends on the effective Coulomb interaction U_{eff} = 3.99 eV. A spin-polarized antiferromagnetic (AFM) structure was adopted for all of total energy and phonon calculations. During the total energy calculations, a plane-wave energy cutoff of 500 eV and a *k*-point mesh of $11 \times 11 \times 11$ with Monkhorst–Pack scheme for twelve-atom unit cell were employed. Accurate total energy calculations are performed by means of the linear tetrahedron method with Blöchl's correction [20]. In all cases the total energies are converged to 10^{-7} eV/cell. Previous studies show that spin–orbit interaction (SOI) has only a minor effect on the ground state structural properties and phonon density of state (DOS) of UO_2 [13]. Therefore we neglected SOI in this work. The occupation matrix control (OMC) scheme proposed by Dorado et al. [16] and the controlled symmetry reduction (CSR) method used by Gryaznov et al. [21] were adopted in this work to search for the ground state among possible meta-stable solutions within DFT+*U* calculations.

The phonon spectra and DOS of UO_2 were calculated by the direct approach as implemented in Yphon code [22]. The Born effective charge tensor and electronic dielectric constant tensor were calculated using the linear-response method as implemented in VASP 5.2. The force constant matrix was calculated in real space using the density functional perturbation theory (DFPT). To obtain accurate force constants, an energy cutoff of 500 eV and $3 \times 3 \times 3$ *k*-point mesh for the $2 \times 2 \times 2$ supercell were used. All the calculated force constants within the supercell were used for the real-space component of the force constants (see Ref. [22] for more details).

3. Results and discussion

3.1. Ground state properties

Before we study the phonon property and free energy, we first benchmarked our calculation of the ground state property of the UO_2 by comparing with previous experimental and theoretical results. Consistent with previous first-principles calculations [13], both LDA and GGA calculations predict a metallic ferromagnetic phase of UO_2 instead of the observed semiconducting AFM phase by experiment. For comparison, LDA+*U* and GGA+*U* methods are able to predict a band gap of about 2.0 eV from the calculated electronic band structure.

The fully relaxed AFM UO_2 phase shows a slightly distorted tetragonal structure, with c/a less than 1. Since the distortion is so small, we keep the cubic structure for the following elastic constant and phonon calculations. To calculate the equilibrium properties, we fitted the calculated total energy vs. volume data by the third-order Birch–Murnaghan equation [23,24]. The obtained equilibrium properties, including the lattice parameter (a), bulk modulus (B), pressure derivative of bulk modulus (B'), Debye temperature (θ_D), are listed in Table 1. Similar to previous DFT calculations [13,14], LDA calculations underestimate the lattice parameter of UO_2 and therefore significantly overestimate the bulk modulus, while GGA calculations provide better prediction of the lattice constant and bulk modulus. We want to point out that our previous studies show that LDA is more accurate in predicting the ground state properties of alkaline metal or transition metal oxides than GGA does [22,25]. The difference might be ascribed to the *f* electrons existed in actinide oxides. However, by including the Hubbard term, the lattice parameter and bulk modulus predicted by LDA+*U* improve considerably, while GGA+*U* calculations seems over correct the lattice constant and predict a less dense structure.

Table 1
Calculated equilibrium lattice parameters (in Å), bulk modulus (in GPa), pressure derivative of bulk modulus, elastic constants (in GPa), and Debye temperature (in K) of UO_2, together with results from previous experimental and theoretical studies.

Method	a (Å)	B (GPa)	B'	C_{11}	C_{12}	C_{44}	θ_D (K)
LDA	5.279	227.8	5.73	440.6	141.3	88.1	432
GGA	5.411	183.3	3.93	369.4	112.5	61.7	391
LDA+*U*	5.449	220.6	4.18	382.3	136.5	64.5	395
GGA+*U*	5.549	192.2	4.15	343.1	121.3	62.7	383
Expt.[a]	5.473	209	4.69	389.3	118.7	59.7	385
LDA+*U*[b]	5.448	220.6	–	380.9	140.4	63.2	399
LDA+*U*[c]	5.447	222.4	–	389.3	138.9	71.3	398.1

[a] Ref. [6].
[b] Ref. [13].
[c] Ref. [27].

In addition, we evaluated the elastic constants of UO_2 using an efficient stress–strain method [26]. The single-crystal elastic constants were determined mainly based on the applied strains of ±0.01. Auxiliary strains of ±0.007 and ±0.013 were also tested, and the differences are less than 1.0%. Table 1 summarizes the predicted elastic constants of UO_2 by LDA, GGA, LDA+*U* and GGA+*U*. Consistent with the predicted lattice constants, the elastic constants by LDA are highly overestimated, while those by GGA are close to experimental data [6]. By adding the Hubbard term, the elastic constants predicted by LDA+*U* show the best agreement with experimental data among all the methods. The LDA+*U* predicted C_{11} and C_{44} are very close to experiments [6], while C_{12} is overestimated about 15%. From the calculated elastic constants, we also estimated the Debye temperature of UO_2. The predicted Debye temperature by LDA+*U* is 395 K, in good agreement with experimental result of 385 K [6]. In the following work, we decide to use only LDA+*U* method for the phonon calculations.

3.2. Phonon property

For the fluorite structure, there are three atoms in the primitive cell; thus, there should be total nine phonon modes, i.e., three acoustic modes and six optical modes. From the group theory, the optical modes at the Γ point belong to the following irreducible representations,

$$\Gamma_{\mathrm{opt}} = T_{1u}(\mathrm{LO}) + T_{1u}(\mathrm{TO}) + T_{2g}, \quad (1)$$

where the symbol u represents infrared active, and g Raman active, respectively. Both T_{1u} and T_{2g} phonon modes are triply degenerate. In Table 2, we compare the calculated Γ-point optical phonon frequencies of UO_2 with the experimental measurement by inelastic neutron scattering [9]. The relative errors for most of the phonon modes are small, less than 6%.

Furthermore, we studied the full phonon dispersion relations in the Brillouin zone of UO_2 at its theoretical equilibrium volumes, as shown in Fig. 1. The phonon dispersion relations of UO_2 have been

Table 2
Calculated phonon frequencies (in THz) of UO_2 at the Γ point together with results from experimental measurement [9].

Mode	This work	Experiment
T_{1u}(LO)	16.72	16.64
T_{1u}(TO)	8.95	8.49
T_{2g}	14.19	13.40

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