Journal of Nuclear Materials 492 (2017) 269–278

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

DFT+U study of the structures and properties of the actinide dioxides

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ARTICLE INFO

Article history:
Received 6 March 2017
Received in revised form
18 May 2017
Accepted 19 May 2017
Available online 23 May 2017

Keywords:
DFT+U
Non-collinear magnetism
Transverse
Longitudinal
Actinide dioxide
Nuclear fuel

ABSTRACT

The actinide oxides play a vital role in the nuclear fuel cycle. For systems where current experimental measurements are difficult, computational techniques provide a means of predicting their behaviour. However, to date no systematic methodology exists in the literature to calculate the properties of the series, due to the lack of experimental data and the computational complexity of the systems. Here, we present a systematic study where, within the DFT+U formulism, we have parametrized the most suitable Coulombic (U) and exchange (J) parameters for different functionals (LDA, PBE, PBE-Sol and AM05) to reproduce the experimental band-gap and lattice parameters for ThO_2, UO_2, NpO_2, PuO_2, AmO_2 and CmO_2. After successfully identifying the most suitable parameters for these actinide dioxides, we have used our model to describe the electronic structures of the different systems and determine the band structures, optical band-gaps and the Bulk moduli. In general, PBE-Sol provides the most accurate reproduction of the experimental properties, where available.

We have employed diamagnetic order for ThO_2, PuO_2 and CmO_2, transverse 3k antiferromagnetic order for UO_2 and AmO_2, and longitudinal 3k antiferromagnetic order for NpO_2. The $Fm\bar{3}m$ cubic symmetry is preserved for diamagnetic ThO_2, PuO_2 and CmO_2 and longitudinal 3k NpO_2. For UO_2 and AmO_2, the transverse 3k antiferromagnetic state results in $Pa\bar{3}$ symmetry, in agreement with recent experimental findings. Although the electronic structure of ThO_2 cannot be reproduced by DFT or DFT+U, for UO_2, PuO_2, NpO_2, AmO_2 and CmO_2, the experimental properties are very well represented when $U = 3.35$ eV, 6.35 eV, 5.00 eV, 7.00 eV and 6.00 eV, respectively, with $J = 0.00$ eV, 0.00 eV, 0.75 eV, 0.50 eV and 0.00 eV, respectively.

1. Introduction

The study of the actinides is primarily due to their importance in the nuclear fuel cycle [1–3], where actinides are commonly encountered in their oxide form (AnO_2) [4–6]. Compared to the metal, the oxides demonstrate better thermal and chemical stability [7], which is of paramount importance when we are considering nuclear energy applications [5]. The oxides enable higher operating temperatures and guard against further oxidation of the nuclear fuels, thus limiting the risk of containment failure and thermal excursion, and ensuring the stability of spent nuclear material for long-term storage [3,4,8]. It is, however, known, that under specific conditions, the AnO_2 may form hyperoxides of the form AnO_{2+x} [9].

In nuclear fission, fissile isotopes of uranium (^{235}U) and plutonium (^{239}Pu) are used as nuclear fuel [3,10]. Over time the composition of nuclear oxide fuels change, either because of the genesis of irradiation-induced defects [11], or because of the formation of fission products [12]. Actinide oxides of interest include thorium dioxide (ThO_2), neptunium dioxide (NpO_2), americium dioxide (AmO_2), and curium dioxide (CmO_2). Evaluating the properties of these materials has important implications for the development of new processing strategies and the storage of nuclear material, thus improving the generation and safety of nuclear energy [10,12–16].

The study of AnO_2 properties faces several challenges. The actinides are inherently unstable, highly toxic, and, due to the risk of nuclear proliferation, subject to strict regulatory controls [17]. In addition, their experimental investigation is further limited by their low abundance, isolation, and high radioactivity, which has led to

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http://dx.doi.org/10.1016/j.jnucmat.2017.05.025

the lack of precise information on fundamental properties [10,18]. Important properties that require assessment include the lattice constants, band gaps, magnetic states, and the bulk moduli. Theoretical chemistry represents a powerful tool to unequivocally determine these properties, although conventional computational methods, based on density functional theory (DFT), often fail due to the relativistic influences and the highly correlated nature of these materials [19]. Hence, treatment by specific methods that are able to asses this type of material is required.

The following methods have been developed to calculate highly correlated materials: the self-interaction correction method (SIC) [20], modified density functional theory (DFT+U) [20,21], dynamic mean field theory (DMFT) [22], and screened hybrid density functional theory (HSE) [23,24]. Among these methodologies, DFT+U represents one of the more computationally tractable means of study, since it offers the possibility to accurately reproduce the properties of highly correlated materials at a reasonable computational cost [1]. This is achieved by manipulating the so-called Hubbard Coulombic (U) and exchange (J) modifiers, thus minimizing the DFT self-interaction error (SIE). However, U and J have to be fitted to experimental data, and for actinide materials, relativistic effects must also be taken into account. This is the reason why, to the best of our knowledge, few theoretical reports have been published so far that consider SOI and noncollinear magnetic order [25–27]. Hence, determining an accurate value of U and J would represent a significant advance, allowing in the exploration of these materials.

In this paper, we perform a systematic study to determine a set of Hubbard parameters for the DFT+U approximation for different functionals and different materials. Past studies have so far limited themselves to discussion of LDA, PW91, PBE or hybrid functionals. To the authors' knowledge, this is the first study of the AnO_2 systems that investigates the performance of the more current AM05 and PBE-Sol functionals. In previous work in the literature, these functionals have been shown to improve calculations of transition metal complexes in terms of the lattice constant and surface energetics [28,29]. It is thus important that their application to AnO_2 systems is evaluated as well. In addition, we have chosen to implement the magnetic state determined from experimental procedure and/or predicted from the one electron crystal field (CF) and Russel-Saunders coupling scheme [25]. Our paper aims to address the issues encountered in the computational modelling of actinide-based materials to provide a basis on which further research can be built.

1.1. *Magnetic structure*

In Fig. 1, under standard conditions, the AnO_2 crystallise in the calcium fluorite (CaF_2) structure with $Fm\overline{3}m$ (No. 225) symmetry [14,30–33]. The lattice resembles that of an actinide face-centred cubic (FCC) structure where oxygen occupies tetrahedral holes. Thus, each actinide (An^{4+}) cation is coordinated to eight oxygen anions (O^{2-}) and each O^{2-} is coordinated to four An^{4+}.

The electronic structure of these materials can be understood from the crystal field (CF) theory. The spin-orbit interaction (SOI) forces the splitting of the single electron *f*-orbitals into two different levels, with $j = 7/2$ and $j = 5/2$ respectively. Since each actinide cation has a cubic environment, the degeneracy of these levels is subsequently broken due to the crystal field. Although this approximation is technically valid only for the single *f*-electron case, it is widely used to predict the orbital occupancy [25]. Hence, Th^{4+}, Pu^{4+}, and Cm^{4+} are predicted to have no effective magnetic moment ($\mu_B = 0$), whereas U^{4+}, Np^{4+}, and Am^{4+} present an effective magnetic moment ($\mu_B \neq 0$), as illustrated in Fig. 2.

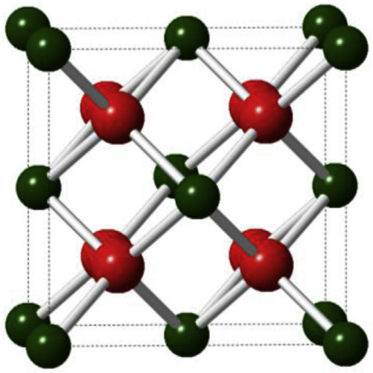

Fig. 1. Representation of the unit cell of an actinide dioxide (AnO_2). An^{4+} ions are coloured in green and O^{2-} ions are coloured in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The display of these magnetic moments in the actinide dioxides leads to different magnetic structures. If the ions show no magnetic moment, the resulting structure is the non-ordered diamagnetic (DM) state. In contrast, if the ions do present an effective magnetic moment, we can have two different situations, depending on whether these magnetic moments are coupled or not. If they are decoupled, there is no ordered distribution and this results in the disordered paramagnetic (PM) phase; if ordered or coupled, either ferromagnetic (FM) or antiferromagnetic (AFM) states are obtained. In addition, if magnetic moments are coupled but they show different μ_B, the resulting magnetic structure is known as the ferrimagnetic (FI) state.

Further, the ordered magnetic AnO_2 exhibit non-collinear behaviour [34–37], where the magnetic moments of the ions have contributions in more than one direction. Hence, we distinguish 1k (one wave-vector), 2k (two independent wave-vectors), and 3k (three independent wave-vectors) magnetic wave vectors [37,38]. Specifically, AnO_2 are non-collinear 3k AFM materials. For the AFM 3k phase, one can distinguish between three different phases: the longitudinal 3k AFM, and the two equivalent transverse 3k AFM domains (A and B), depicted in Fig. 3.

The non-ordered magnetic systems are relatively simple to calculate compared to their ordered non-collinear magnetic counterparts. Experimentally, for ThO_2 [39] and PuO_2 [40–44] diamagnetism has been confirmed. It is worth noting, however, that there is a controversy over the exact magnetic ground state for PuO_2, where first-principles methods have suggested the possibility of an AFM ground state [25]. However, for this work we have assumed the DM ground state, as supported by the complete active space self-consistent field (CASSCF) [45] method and experimental evidence [40,42–44]. CmO_2 has been reported as PM, although according to CF theory, it should be DM. It is believed that the presence of impurities plus the small energy difference between the DM and the PM phases in CmO_2 are the reason the DM phase has been difficult to determine [12,46]; here, we have again assumed a DM ground state for CmO_2.

The ordered magnetic AnO_2 have attracted considerable interest, in part due to their non-trivial multi-k and multipolar nature. In UO_2, the magnetic ground state is identified as a transverse 3k AFM [47] state at $T_N = 30.8$ K [48] (where T_N is the Neel Temperature for an AFM-PM magnetic transition) with a corresponding effective magnetic moment of 1.74 μ_B/U ion. In addition, neutron studies have indicated an internal oxygen displacement; although no external distortion of the cubic structure occurs [49]. One theoretical study has employed SOI to investigated the relative