SIMULATION OF POSITRON LIFETIMES IN URANIUM DIOXIDE: AN *AB INITIO* STUDY

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1. Introduction

Uranium dioxide (UO_2) attracts scientific attention especially in two areas: From industrial point of view, UO_2 is standard fuel material used in fission reactors. From theoretical point of view,UO_2 is Mott-Hubbard isolator with strong correlated f-electrons in valence sphere. Next paragraph will contemplate each scope in detail.

Nuclear fuel undergoes during power plant operation a radiation damage, which is connected with generation of different types of crystalline structure defects. Understanding of radiation damage effects on nuclear fuel is a question of a high importance, concerning the safety of nuclear power plant operation. The density functional theory (DFT) simulations offer the valuable microscopic theoretical insight on this problem [1-3]. On the other hand positron annihilation lifetime spectroscopy (PALS) can be used for experimental study of vacancy type defects generated in material. Introduction of the second component (positron) into DFT by Boroński and Nieminen [4] enabled to simulate positron lifetimes in solids and use computer simulations for refinement of PALS spectra. The approach is called two-component DFT (TC-DFT). The availability of experimental PALS measurements on UO_2[5-7] as well as numerical calculations of positron lifetimes in UO_2 is very limited [8]. Correct prediction of electronic structure is essential for positron lifetime simulation, while the positron lifetime depends on the distribution of electronic and positron charge density. The strong correlated U-5f electrons represent a big challenge for electronic structure calculations. Within the DFT, there are two types of approximations used to describe exchange-correlation interaction of electrons. It should be noted that neither local density approximation (LDA) nor generalized gradient approximation (GGA) is able to correctly describe specific properties of f-electrons. For example UO_2 is a semiconductor with band gap around 2eV [9]. In order to achieve semiconductor state of UO_2 by DFT simulation a special correction has to be included. The correction based on addition of a Hubbard term to the Hamiltonian, referred as DFT+U [10-12],proved to be appropriate tool to handle with this problem. However, this method yields to a multiple local minima in which the system can be trapped[13]. This difficulty can be overcome by careful control of occupation of U-5f orbitals or by continuously increasing of U and J parameters, added by DFT+U to Hamiltonian, up to requested values, which ensure the correct semiconductor state. The first method is known as occupation matrix control (OMC) scheme [13,14] and the second one as U-ramping scheme [15].

In this paper we present the electronic structure of UO_2together with positron lifetimes related to O-type point defects in UO_2. The paper is organized as follows: The theory of TC-DFT is presented in Sec. 2; details of our numerical experiment are described in Sec. 3; main results are summarized in Sec. 4 and discussed in Sec.5.

2. Two-component density functional theory

Positron lifetime in specific material depends on its electronic structure. Each defect breaks the ideal crystalline structure and hence is responsible for change in electronic density distribution. Positron, as a particle with positive charge, has the tendency to localize in vacancy regions, where are no positive ions located. Positron lifetime increases with decreasing overlap of electronic and positron charge density.This in fact can be determined as

$$\tau = 1/\lambda \tag{1}$$

where

$$\lambda = \frac{\pi {r_0}^2 c}{e^2} \int n^+(r)^2 n^-(r)^2 \gamma(n^+, n^-) dr \tag{2}$$

The annihilation ratioλ depends on$n^+(r)$and$n^-(r)$, which are distributions of positron and electronic charge density respectively. Constant $r_0$is classical electron radius, c is speed of light, e is elementary charge and $\gamma(n^+, n^-)$ is enhancement factor. To calculate positron lifetime both, electronic and positron charge density distribution is needed and therefore the TC-DFT approach is necessary. Within the TC-DFT technique the TC-Schrödinger equation for positron (Eq.(3)) and TC-Schrödinger equation for electrons (Eq.(4))

$$\left\{-\frac{1}{2}\Delta^2 + V_{ion}(r^+) + V_H^{e-p}(r^+) + V_{corr}^{e-p}(n^-, n^+)\right\}\psi^+(r^+) = E^+\psi^+(r^+) \tag{3}$$

$$\left\{-\frac{1}{2}\Delta^2 + V_{ion}(r^-) + V_H^{e-e}(r^-) + V_{xc}(n^-) + V_H^{e-p}(r^-) + V_{corr}^{e-p}(n^-, n^+)\right\}\psi^-(r^-) = E^-\psi^-(r^-) \tag{4}$$

are solved self-consistently. Indexes $(-)$ and $(+)$ refer to electron and positron respectively. PotentialV_{ion} is ionic potential, V_H is Hartree potential, V_{xc} is exchange potential and V_{corr} is correlation potential. There is no positron exchange-correlation term for positron in Eq.(3) because only one positron in a cell at a given time is considered. In order to compute positron lifetime properly, the definition of enhancement factor γ is crucial (see Eq.(2)), while the presence of positron in material also influences the electron density charge distribution. Enhancement factor describes the increase of electron density in a presence of positron due to the attractive coulomb interaction. This phenomena is called screening effect. There are several parametrizations according to definition of enhancement factor. First parametrizations [4,16,17] were based on LDA approximation, where the exchange-correlation functional is derived for homogenous electron gas. This approximation is suitable for systems with slow varying electron density – metals, where the screening effect is strong. In a case of semiconducting and isolating materials the screening effect is reduced due to the existence of band gap. Apart from that, LDA approximation leads in general to over-correlation of electrons and positron and hence to low values of positron lifetimes. To improve the predicting power of positron lifetime calculations and description of screening effect in non-metallic materials gradient correction was introduced[18, 19].

3. Numerical experiment

Our numerical experiment consists of two parts. In the first part the pseudopotentials were tested and band structure of UO_2 was computed to ensure, that correct semiconductor state was obtained. After that positron lifetimes for bulk, O-vacancy and O-interstitial were computed. Numerical calculations were carried out by the PAW[20] formalism as implemented in ABINIT[21] code. PAW potential for uranium was generated in ATOMPAW[22] code and PAW potential for oxygen is available in ABINIT pseudopotential repository. We employed both, LDA (Pedrew-Wang 92) and GGA (Pedrew-Burke-Ernzerhof) exchange-correlation functional. In order to take into account the strong

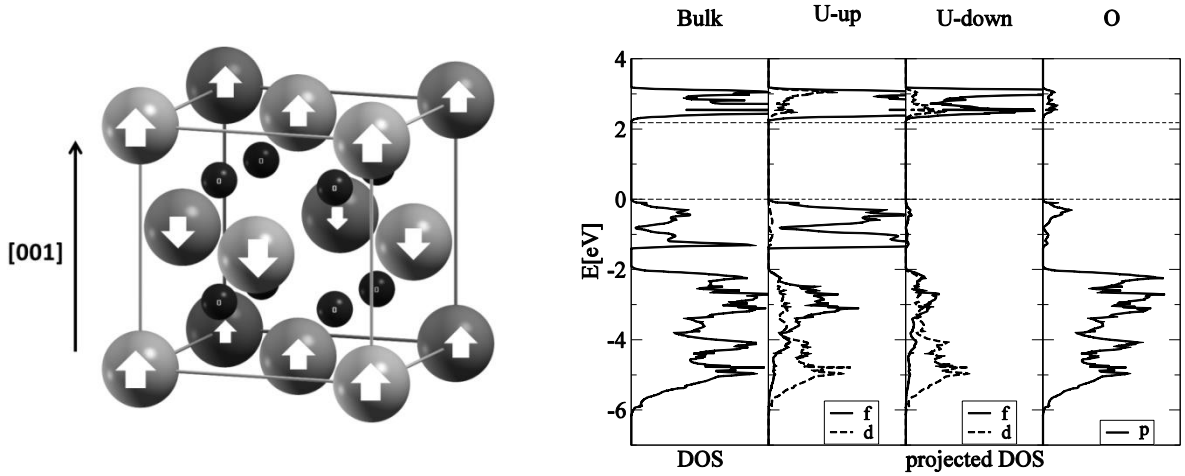
correlation of U-5f electrons the DFT+U approach was applied with U and J parameters set up to 4.5eV and 0.51eV respectively. The values of U and J wereadopted fromDudarev et al.[23]. For the test of pseudopotentials and band structure calculation the U_4O_8 supercell with 1k-antiferomegnetic ordering in direction [001] was used (see Fig.1a). K-point space was sampled by 6x6x6 Monkhorst-Pack (MP) set, which corresponds to 18 k-points. The cut-off energy of plane wave set was set to 1632eV and fine FFT grid cut-off was set to 2721 eV. In order to reach ground state, the OMC scheme was applied. It must be emphasized that the occupation matrix was not obtained in traditional way by testing of several occupancies of U-5f electrons. The occupation matrix used in OMC scheme was obtained by U-ramping scheme applied on U_4O_8supercell with fixed experimental value of lattice parameter 5.46Å. Band structure was calculated by GGA functional with neglected distortion of lattice parameter in [001] direction. The positron lifetime computations were performed on(2x2x1) $U_{16}O_{32}$ supercell. Plane wave energy cut-off and fine FFT grid cut-off were reduced to 1088 eV and 1632 eV respectively from computational reasons. A specific supercell was constructed to introduce O-interstitial and O-vacancy. For the O-interstitial the octahedral position in the centre of the oxygen cube was taken into account. K-point space was sampled by 4x4x6 MP set corresponding to 9 k-points for bulk and 2x2x4 MP set corresponding to 8 k-points for cells with inserted defect. For the LDA enhancement factor the Puska-Seitsonen-Nieminen parametrization [17] was used and for GGA the Sterne-Keiser parametrization [16] with gradient correction was used. The same occupation matrix as in case of band structure calculation was applied for defected as well as non-defected supercells.

4. Results

Basic parameters of UO_2 obtained by LDA as well as GGA DFT simulation are summarized in Tab. 1. The relative dilatations of simulated parameters from experimental values are within the range standardly achieved by precise DFT simulations. While the presence of antiferromagnetic ordering breaks the cubic symmetry, the band structure according the simple cube path ΓXMΓRX in the 1st Brillouin zone was calculated for X point lying in [010] direction - X_a(Fig.2a) and X point lying in[001] direction - X_c (Fig.2b). The non-equivalence of points X_a and X_c is clear from band structure along path ΓXM|RX.The top of valence band lies in X_c point and the bottom of conduction band is located in R point. Projected DOS for U-5f spin up electrons and O-2p spin up electrons are in Fig. 1b. The top of valence band is created from U-5f and O-2p electrons. It indicates U(5f)-O(2p) bonding. Moreover the comparison of projected DOS between U atoms with magnetic moment oriented up and down confirms that U-5f electrons are also responsible for antiferromagnetic ordering. Conduction band consists mainly from U-5f orbital.

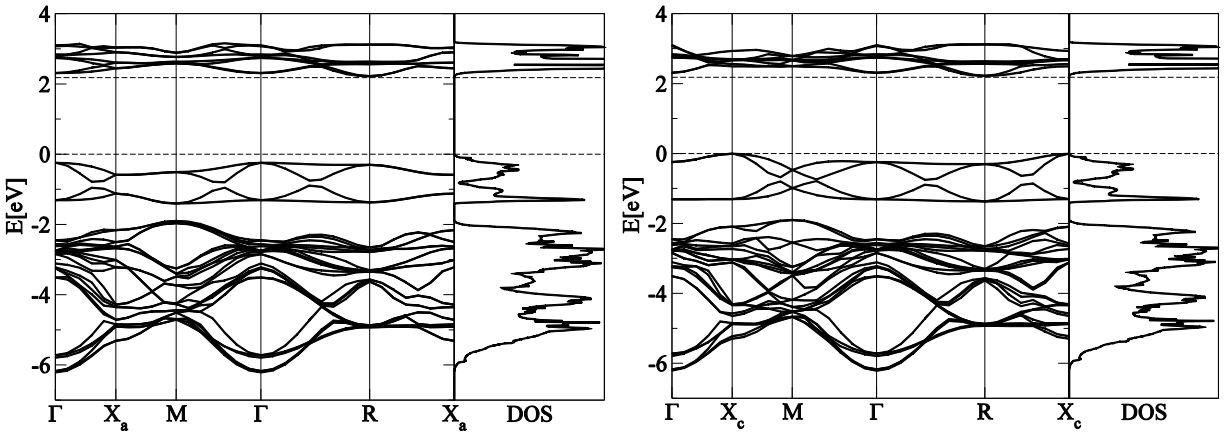
Tab. 1. *Basic parameters of UO_2obtained by our DFT simulation andcompared to experiment. a, c – lattice parameters, B – bulk modulus, E_c – cohesive energy, E_g – band gap, m – magnetic moment of U atoms.*

parameter	LDA	GGA	experiment[9,25-27]	δ_{LDA}[%]	δ_{GGA}[%]
a[Å]	5.45	5.54	5.46	-0.18	1.47
B[GPa]	222	193	207	7.25	-6.89
E_c[eV/UO_2]	-22.13	-21.98	-22.31	-0.80	-1.47
E_g[eV]	1.96	2.3	1.8 - 2.1	in range	above range
m[μ_B]	1.69	1.71	1.74	-2.87	-1.72
c[Å]	5.428	5.515	-	-	-
c/a	0.996	0.995	-	-	-



a) b)

Fig.1: *a) Simulation cell U_4O_8 with 1-k antiferromagnetic ordering in [001] direction; b) Total and projected DOS for spin-up component. U-up and U-down represents uranium atom with magnetic moment oriented up and down respectively according the Fig.1a.*



a) b)

Fig.2: *a) Band structure ofUO_2alongside path ΓXMΓRXwith X point lying in [010] direction; b) Band structure of UO_2 alongside path ΓXMΓRXwith X point lying in [001]direction. Fermi energy is set up to 0 eV.*

Positron lifetime in a bulk UO_2 calculated by LDA and GGA is 141 psand 171 ps respectively. The value calculated by GGA is in good agreement with experimental one (168 ps) as well as simulation made by Wiktor et.al (167 ps) [8]. Low bulk lifetime obtained by LDA is consistent with the tendency of LDA to over-estimate electron-positron correlation, as it was mentioned in Sec. 2. Presence of O-interstitial in octahedral position reduces the lifetime by 5 ps in comparison to bulk. As a consequence, eventually measured bulk component lower than 170 ps, could mean the oxygen over-stoichiometry of UO_2 sample. Wiktor et al. reported the lifetime for O-vacancy 206 ps, which is about 39 ps higher then bulk lifetime. Our simulation shows that the presence of O-vacancy leads to lifetime 19 ps higher than bulk lifetime. The 20 ps discrepancy is most probably caused by neglected atomic relaxation in our simulation. It is generally known that the ionic relaxation around defects plays crucial role in predicting defect properties in semiconductors. It was shown that the presence of positron in open-volume defect reduces the amount of relaxation; nevertheless the influence of relaxation on positron lifetime is not negligible [24] and for accurate estimation of positron lifetimes should be included. Moreover the fact that for O-vacancy and LDA approximation was reached no convergence supports the idea, that GGA is much better in description of materials with sharp changes in electron density. Despite

neglected relaxation, it was shown that lifetime connected with O-interstitialis shorter than lifetime connected with O-vacancy.

5. Conclusion

We have performed numerical simulation of UO_2 band structure and positron lifetimes of bulk, O-vacancy and O-interstitial. Band structure proved that UO_2 bonding is realized by U-5f and O-2p electrons. Antiferromagnetic ordering implies non-equivalent band structure along [010] and [001] direction. Top of valence band is located atX_c point (lying in [001] direction) and bottom of conduction band in R point. Antiferromagnetic ordering is driven by U-5f electrons. GGA approximation showed better stability in convergence during the simulation of positron lifetimes. Bulk lifetime 170ps is very close to experimental value 168 ps. Addition of O-intestinal reduces positron lifetime by 5 ps. The consequence of over-stoichiometric UO_2 could be a little bit reduced bulk lifetime component.In a case of O-vacancy a relatively big discrepancy between our simulation 190 ps and the one performed by Wiktor et al. 206 ps is observed. Wiktor et al. considered the full relaxation while we not. In order to use our results for reliable interpretation of PALS spectra full atomic relaxation in a presence of positron has to be added. This will be the subject of our future research.

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