Local structure and cohesive properties of mixed thorium and uranium dioxides calculated by "ab initio" method

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Abstract. Density functional theory (DFT) results of calculations of the mixed thorium and uranium dioxide $Th_{1-x}U_xO_2$ for the following mole ratio $x = 0, 0.25, 0.75$ and 1 are presented and discussed. "Ab initio" calculations were performed using the Wien2k program package. To compute the unit cell parameters the 12 atom super-cell were chosen. The lattice parameters were calculated through minimization of the total energy by the change of lattice parameters and atom displacement within the unit cell. Calculations were performed for five different exchange energy approximations E_{XC} with and without corrective orbital potential U, and obtained lattice constants are presented graphically and compared with experimental data. It is established that the initially assumed oxygen location within the unit cell ± 0.25 of the mixed compounds are not their equilibrium positions. The oxygen atoms within the unit cell undergo dislocation in the (111) direction. So, the distances oxygen-uranium are smaller than the distances oxygen-thorium. The change of local structure is presented graphically and appropriate parameters values are given in Table. The bulk modulus and the cohesive properties are also counted and shown graphically.

Key words: uranium • thorium dioxide • DFT+U • LDA • GGA • local structure • cohesive properties • bulk modulus

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Introduction

In the past decade there has been a renewal of interest in studying the feasibility of thorium-based fuel reactors as a potential advanced fuel for Generation IV nuclear energy systems producing fewer minor actinides than in uranium based-fuel.

[232]Th is a better fertile material than [238]U in thermal reactors because of three times higher thermal neutron absorption cross-section of [232]Th (7.4 barns) as compared to [238]U (2.7 barns). Thus, the conversion of [232]Th to [233]U is more efficient than that of [238]U to [239]Pu in thermal neutron spectrum though the resonance integral of [232]Th is one third of that of [238]U [9].

Conversion of thorium-232 and uranium-233 under neutron irradiation leads in the fertile fuel of thorium dioxide to form mixed dioxide $Th_{1-x}U_xO_2$ for x ranging from 0 to 1.

The uranium dioxide and thorium dioxide properties attract attention of many researchers for many years now. In the last decade the numerical method "ab initio" based on the density functional theory (DFT) [7, 10] is more and more often used. The method let us to obtain additional information of lattice constant, cohesive energy, bulk modulus, magnetic properties and etc. In the case of UO_2 the information can be found in [11, 12], and regarding ThO_2 in a paper [13]. Research of mixed thorium and uranium dioxide is dedicated to the

experimental work [8] investigating the local structure of mixed dioxide compounds $Th_{1-x}U_xO_2$ for many mole ratio x ranging from 0 to 1 in the aspect of crystal lattice constant change and the local atomic structure around uranium and thorium atoms.

As the papers concerning the calculation by "ab initio" method in the open literature are limited to UO_2 or ThO_2. So, the focus of our work is the local atomic structure around Th and U, and unite cell parameters in the mixed thorium and uranium dioxides for different mole ratio x what can influence the volume of fuel pellets since there is connection between atomic and macroscopic levels. The prediction of evolution of the fuel volume is crucial in determining fuel performance in future reactors. In order to increase the reliability of our calculation results we have applied five alternative exchange-correlation energy functional E_{XC} with and without the correlation correction potential U.

Method of calculations

"Ab initio" calculations of the electronic structure were performed using the Wien2k program package [2] based on the density functional theory (DFT). The Kohn-Sham (K-S) total-energy functional is applied here as follows:

$$(1) \quad E[\Psi_i] = 2\sum_i \int \Psi_i^* \left(-\frac{\hbar^2}{2m} \right) \nabla^2 \Psi_i d^3\vec{r}$$

$$+ \int V_{ion}(\vec{r})n(\vec{r})d^3\vec{r} + \frac{e^2}{2}\iint \frac{n(\vec{r})n(\vec{r}')}{|r-r'|}d^3\vec{r}$$

$$+ E_{XC}[n(\vec{r})] + E_{ion}(\{\vec{R}_i\})$$

The first term of Eq. (1) describes the kinetic energy of electrons, in the second term $V_{ion}(\vec{r})$ is the electron-ion potential and $n(\vec{r})$ is the electronic density given by:

$$(2) \quad n(\vec{r}) = 2\sum_i \left| \Psi_i(\vec{r}) \right|^2$$

The third term describes Coulomb electron-electron interaction, the fourth term $E_{XC}[n(\vec{r})]$ is the exchange-correlation energy functional and the fifth term $E_{ion}(\{\vec{R}_i\})$ is the Coulomb energy associated with interaction among the nuclei at positions $\{\vec{R}_i\}$.

The Kohn-Sham equations are solved self-consistently in an interactive process using the linearized augmented plane wave (LAPW) method. A basic set of functions is introduced in two region of the cell. The first region, region I, is the non-overlapping atomic sphere, and region II is the interstitial region.

Inside the atomic sphere t of radius R_t, a linear combination of radial and spherical harmonic $Y_{lm}(r)$ functions are used:

$$(3) \quad \varphi_{k_n} = \sum_{lm} \left[A_{lm,k_n} u_l(r,E_l) + B_{lm,k_n} u_l(r,E_l) \right] Y_{lm}(r)$$

where $u_l(r,E_l)$ is the regular solution of the radial Schrödinger equation for energy E_i and the spherical part of the potential inside sphere t; $u_l(r,E_l)$ is the energy derivative of u_l evaluated at the same energy E_l.

In the interstitial region a plane wave expansion is used

$$(4) \quad \varphi_{k_n} = \frac{1}{\sqrt{\omega}} e^{ik_n.r}$$

where $k_n = k + K_n$; K_n are the reciprocal lattice vectors and k is the wave vector inside the first Brillouin zone.

The total potential in the LAPW method is expanded analogously to the electron densities in the forms:

$$(5a) \quad V^{I}(r) = \sum_{L,M} V_{L,M}(r)Y_{lL,M}(r) \quad \text{inside the atomic sphere}$$

and

$$(5b) \quad V^{II} = \sum_K V_K e^{iK.r} \quad \text{outside the atomic sphere.}$$

Theoretical studies of uranium compounds are difficult due to a relativistic character of electron motion in the U atom core and strong electron-electron correlation. Chemical bonds of uranium in compounds is a complex one and is characterized by a mixed metal-covalent chemical bonding. Taking into consideration the above, in all DFT calculations we use several exchange-correlation energy functional $E_{XC}[n(\vec{r})]$ both within the local spin-polarized density (LSDA) and generalized gradient (GGA) approximations, namely:
1) PBE-GGA
2) WC-GGA
3) PBEsol-GGA
4) GGA
5) LSDA

The above potentials are recommended by authors of Wien2K program package [2].

All the calculation were performed using the Hubbard model (DFT+U), corrective exchange-correlation energy functional $E_{XC}[n(\vec{r})]$.

Unit cell structure and parameters

Compounds ThO_2 and UO_2 are isomorphic, with a face-centered cubic lattice (fcc) of the fluorite type structure, with similar lattice parameters: a = 5.5975 and 5.396 Å, respectively [1]. Replacing the uranium atoms by the thorium atoms in the UO_2 we bring down the symmetry from the initial one Fm-$3m$ (#225) to Pm-$3m$ (#221). Our calculation concerns the following mole ratio x = 0, 0.25, 0.75 and 1 of the mixed dioxide $Th_{1-x}U_xO_2$. The unit cell structures for the mole ratio equal to 0.25 and 0.75 are presented in Figs. 1a and 1b. To compute the unit cell parameters the 12 atom super-cell was chosen. Calculation of lattice parameters, oxygen coordinates and the first two shell distances for the mixed uranium and thorium dioxide are presented in Table 1. Calculations were performed for five different exchange energy approximations $E_{XC}[n(\vec{r})]$, specified in the previous paragraph, with and without corrective orbital potential U for comparison.

While computing, we look for the optimal atom location that ensure a minimum value of total energy. Each time the forces acting on the atoms (ions) are also computed.

The lattice parameters were computed in three stages:
– Stage 1 – minimization of the total energy through the change of lattice parameters (volume).
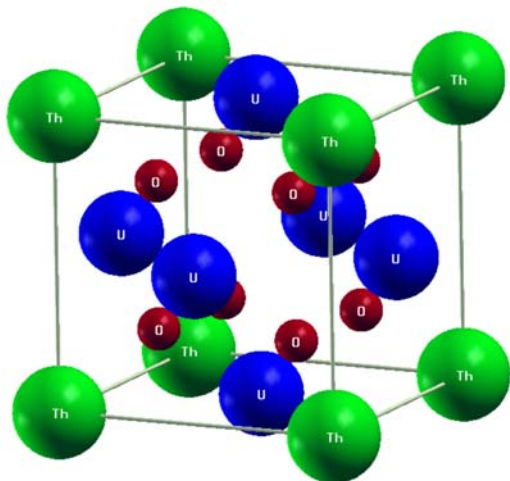
Fig. 1a. Unit cell $Th_{0.75}U_{0.25}O_2$.
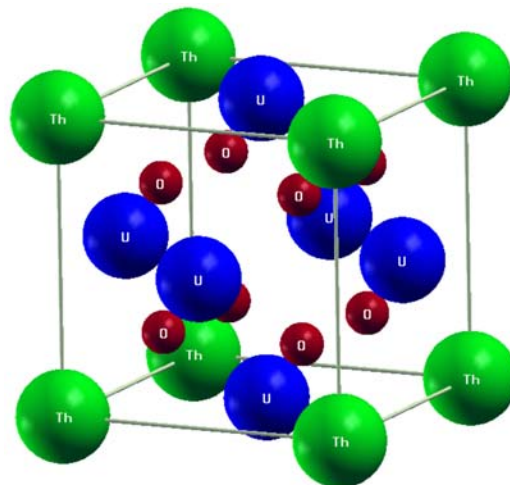
Fig. 1b. Unit cell $Th_{0.25}U_{0.75}O_2$.

Table 1. Lattice parameters, oxygen coordinates and the first two-shell distances for the unit cell $Th_{1-x}U_xO_2$

| E_{XC}	a_0 (Å)	Oxygen coordinates ($x = y = z$)	I shell Th-O (Å)	I shell U-O (Å)	I shell \<met-O\> (Å)	II shell \<met-met\> (Å)
			ThO$_2$			
Exp. [8]	5.5975		2.424			3.959
LDA [11]	5.6360					
GC [13]	5.6620					
LTMO-LDA [13]	5.5230					
LTMO-GGA [13]	5.6110					
PBE-GGA+U	5.6312	± 0.25	2.4384		2.4384	3.9819
LSDA+U	5.5880	± 0.25	2.4197		2.4197	3.9513
WC-GGA+U	5.5667	± 0.25	2.4105		2.4105	3.9363
PBEsol-GGA+U	5.5729	± 0.25	2.4131		2.4131	3.9406
GGA+U	5.6730	± 0.25	2.4565		2.4565	4.0114
			Th$_{0.75}$U$_{0.25}$O$_2$			
PBE-GGA+U	5.6118	± 0.2459	2.4436	2.3901	2.4302	3.9681
LSDA+U	5.5593	± 0.2452	2.4230	2.3620	2.4077	3.9310
WC-GGA+U	5.5515	± 0.2449	2.4207	2.3548	2.4042	3.9255
PBEsol-GGA+U	5.5570	± 0.2448	2.4234	2.3562	2.4063	3.9294
GGA+U	5.6489	± 0.2459	2.4577	2.4059	2.4463	3.9944
			Th$_{0.25}$U$_{0.75}$O$_2$			
PBE-GGA+U	5.5723	± 0.2541	2.4524	2.4000	2.4131	3.9402
LSDA+U	5.5055	± 0.2547	2.4288	2.3680	2.3843	3.8930
WC-GGA+U	5.5207	± 0.2544	2.4326	2.3768	2.3908	3.9037
PBEsol-GGA+U	5.5264	± 0.2544	2.4351	2.3793	2.3933	3.9078
GGA+U	5.5870	± 0.2541	2.4589	2.4063	2.4195	3.9506
			UO$_2$			
Exp. [8]	5.4704					
LDA [11]	5.2500					
GC [13]	5.2700					
LSDA [6]	5.3230					
GGS [6]	5.4320					
LSDA+U [6]	5.4440					
GGS+U [6]	5.5520					
PAW-GGA+U [5]	5.4400					
LDA+U [14]	5.3700					
PBE-GGA+U	5.5526	± 0.25		2.4043	2.4043	3.9263
LSDA+U	5.4693	± 0.25		2.3696	2.3696	3.8674
WC-GGA+U	5.5053	± 0.25		2.3839	2.3839	3.8928
PBEsol-GGA+U	5.5066	± 0.25		2.3844	2.3844	3.8938
GGA+U	5.5508	± 0.25		2.4036	2.4036	3.9250
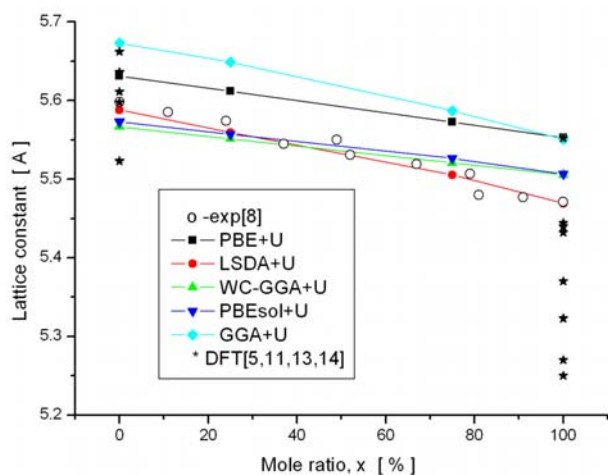
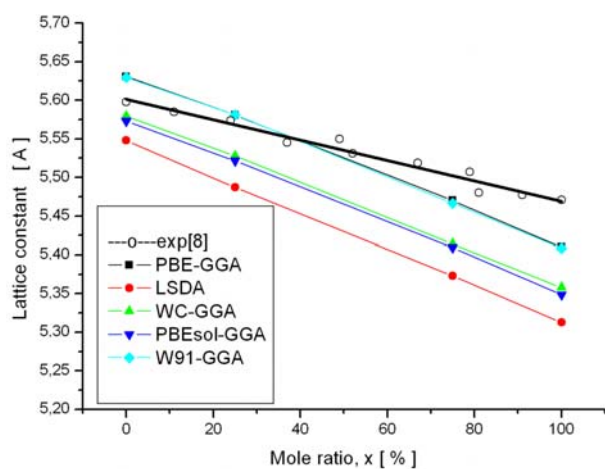**Fig. 2a.** Lattice constant vs. mole ratio for unit cell $Th_{1-x}U_xO_2$ (DFT+U) – other calculations – see Table 1.

Fig. 2b. Lattice constant vs. mole ratio for unit cell $Th_{1-x}U_xO_2$ (DFT).

– Stage 2 – at the obtained equilibrium lattice constants – zeroing of forces acting on the separate atoms in the lattice (Hellman-Feyman forces) through the change of atom coordinates within the unit cell.
– Stage 3 – repetitive minimization of the total energy through the change of lattice parameters (volume).

The values of lattice parameters given in Table 1 are obtained in the final stage – the third stage of calculation.

In Figs. 2a and 2b are presented the calculation results of the lattice constant in function of the mole ratio for the considered unit cell $Th_{1-x}U_xO_2$ for five different exchange energy approximations with and without corrective orbital potential U, respectively and compared with experimental data available in the literature.

Local structure of unit cell $Th_{1-x}U_xO_2$

The ion radius difference of Th^{4+} (1.05 Å) and U^{4+} (0.99 Å) cause that the lattice constants of uranium dioxide are smaller than that of thorium dioxide. In the mixed compounds, as shows the experiment [8], the lattice constant values take on the in-between values. In the process of equilibrium lattice constants determina-
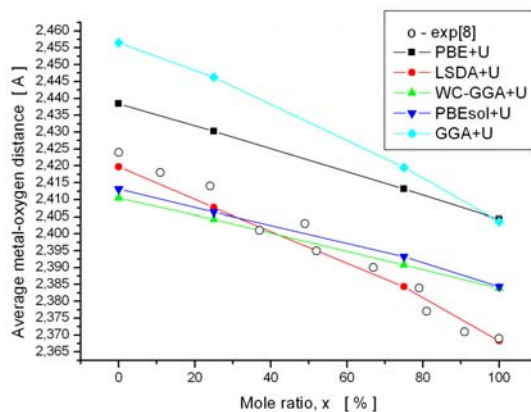

Fig. 3a. Average interatomic distances oxygen-metal for $Th_{1-x}U_xO_2$ (DFT+U).

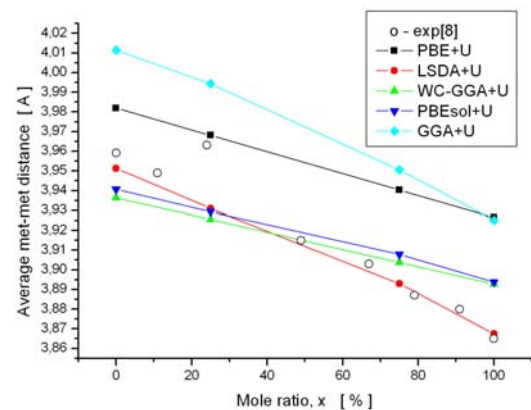**Fig. 3b.** Average interatomic distances metal-metal for $Th_{1-x}U_xO_2$ (DFT+U).

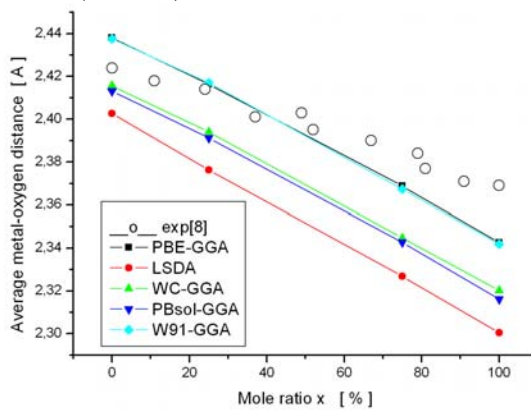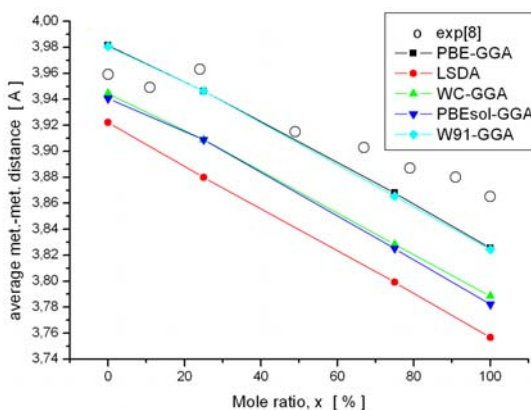**Fig. 3c.** Average interatomic distances oxygen-metal for $Th_{1-x}U_xO_2$ (DFT).

Fig. 3d. Average interatomic distances metal-metal for $Th_{1-x}U_xO_2$ (DFT).

tion it appeared that the initially assumed position of oxygen $x = y = z = \pm 0.25$ in the unit cell of the mixed compounds are not the equilibrium positions. The oxygen atoms within the unit cell undergo dislocation in the (111) direction. So, the distances oxygen-uranium are smaller than the distances oxygen-thorium what was observed in the experimental work [8]. The averaged computed and measured oxygen-metal distances are presented in Fig. 3a, while the metal-metal distances are presented in Fig. 3b. The theoretical equilibrium lattice parameters in Figs. 3a and 3b were obtained using the corrective orbital potential U, while in Figs. 3c and 3d the same dependences are presented but without the potential U in order to comparison.

Cohesive properties of unit cell Th$_{1-x}$U$_x$O$_2$

Application of orbital potential U improves the calculation precision. The potential U is indispensable, especially when we deal with f electrons what takes place in the case of uranium. We calculated the cohesive energy, and bulk modulus with different approximations of exchange-correlation energy functional $E_{\mathrm{XC}}[n(\vec{r})]$. The calculation results of cohesive energies for four mole ratios $x = 0, 0.25, 0.75$ and 1 computed by the DFT+U method is presented in Fig. 4a and compared with other
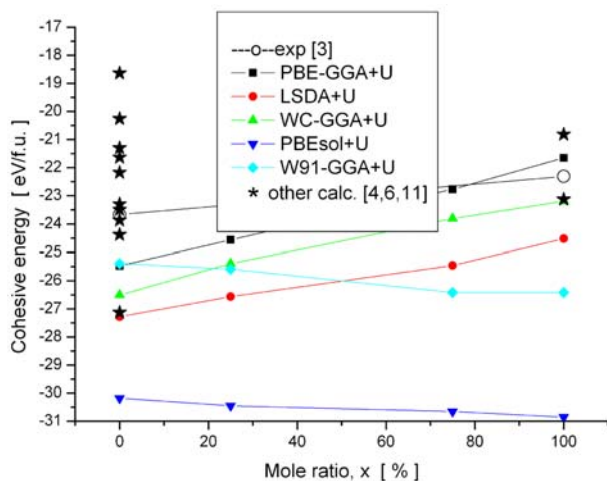
Fig. 5. Variation of the cohesive energy with cell volume for Th$_{1-x}$U$_x$O$_2$ (LSDA+U).
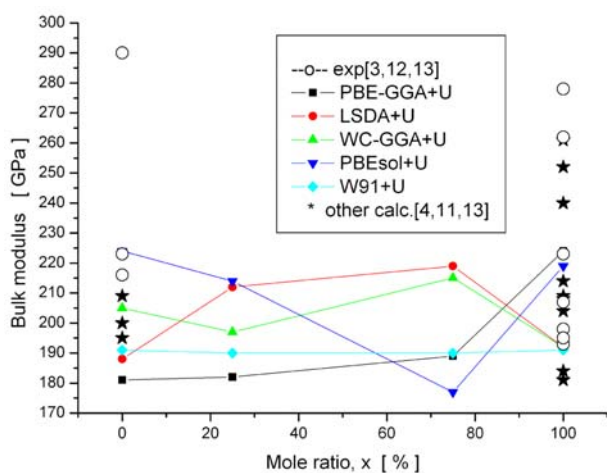
Fig. 6. Variation of the bulk modulus with mole ratio for Th$_{1-x}$U$_x$O$_2$ (DFT+U).

calculations [4, 6, 11] and experimental data [3], while calculated by using DFT method presented is in Fig. 4b together with experimental data [3] for comparison. For the same mole ratios Fig. 5 shows the dependence of cohesive energy on unit cell volume computed by the LSDA+U method. Figure 6 presents our calculation results of bulk modulus also for the same mole ratios computed by the DFT+U method (DFT+U solution) and compared with calculation results of other authors [4, 8, 11, 13] and with experimental data available in the literature [3, 12, 13] as well.

Discussion of results

The obtained values of lattice constants, particularly calculated with the application of orbital potential U (Fig. 2a), are very close to experimental data published in the literature. The best fitting results are the results computed by LSDA+U method which practically are identical with experimental data. The worst fitting points are the GGA+U calculations and they deviate from experimental values by about 1.5%. The best results calculated without corrective orbital potential U are the results obtained from W91-GGA and PBE-GGA calculations which run away from experimental values also by about 1.5%, while the worst by about 3%
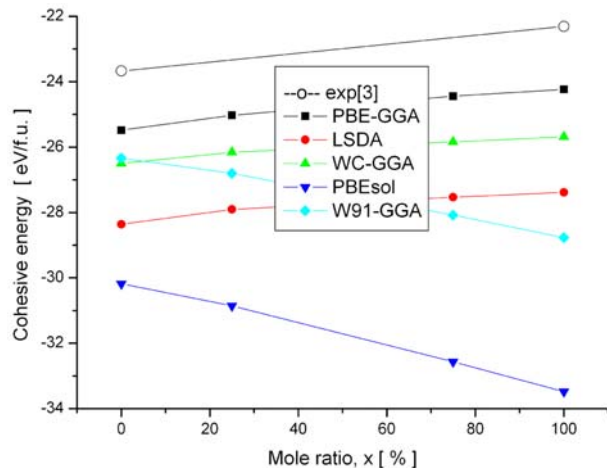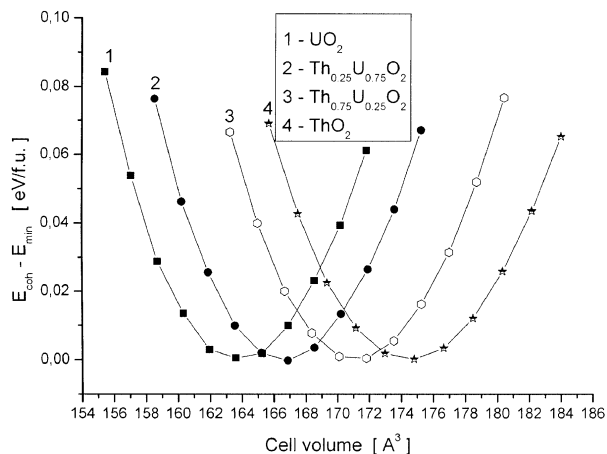
Fig. 4a. Variation of the cohesive energy with mole ratio x for Th$_{1-x}$U$_x$O$_2$ (DFT+U).

Fig. 4b. Variation of the cohesive energy with mole ratio x for Th$_{1-x}$U$_x$O$_2$ (DFT).

in the case of LSDA results. All our computation results are situated within the results of other authors [5, 6, 11, 13, 14]. Comparing the results presented in Figs. 2a and 2b, we noticed the tendency of overestimation the calculated lattice constants when using the potential U and *vice versa* underestimation of its disuse.

These regularities are confirmed also for calculation results of oxygen-metal and metal-metal distances presented in Figs. 3a–3d. The best results, practically overlapping with experimental values, are the results computed by the LSDA+U solution. In the second case when we do not use the orbital potential U, any of the presented oxygen-metal and metal-metal vs. mole ratio dependencies (Figs. 3c and 3d) do not precisely reflect the experimental data. The slope of theoretical curves are different then from the experimental curve.

The extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD), neutron diffraction (ND) and other methods assumed by the authors [8] for investigation of the local structure of actinide solid solutions enable to measure the average distances between the atoms. However, these methods do not allow to measure the local distances between atoms within the unit cell as, for example, in the situation presented in Figs. 1a and 1b. The "ab initio" method provides a possibility to calculate the distances. In Fig. 7 are presented the uranium-oxygen and thorium-oxygen distances (lower and upper curves) as a function of mole ratio obtained in the result of numerical calculations using the LSDA+U potential. It can be expected that the distances do not vary with the mole ratio and their values are as in the pure UO_2 and ThO_2. From Fig. 7 follows that the first approximation is correct according to our expectation but one can also notice that both of the distances slightly increase with mole ratio.

On the basis of hitherto considerations we can conclude that the numerical calculations using the LSDA+U method give the best fitting to the structural experimental data. However, this statement does not concern the cohesive properties what is appeared from Figs. 4a and 4b. In this case the best fitting to experimental data are the calculations when the PBE method is used, and especially the PBE+U one. The accuracy of our cohesive energy calculations lies within the range from 4 to 7% and is not worse than the accuracy reached by other authors [4, 6, 11].
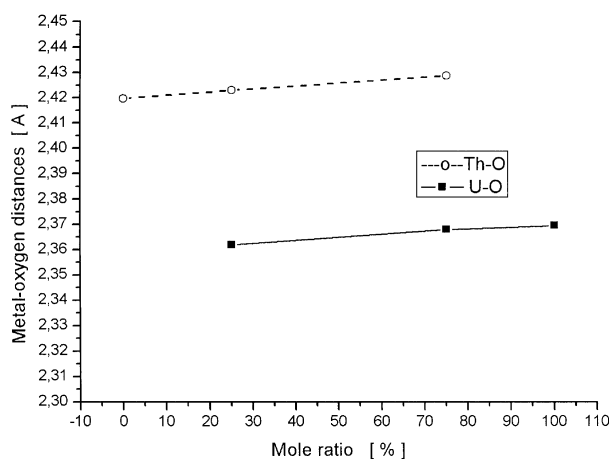
The lowest accuracy concerns the bulk modulus calculations what refers both to our and other authors [4, 8, 11, 13] numerical results. Also the experimental data differ significantly from each other using even the same method. For example, the results [13] of bulk modulus for ThO_2 is equal to 195 GPa and 262 GPa as well when using the same XRD method. The experimental data divergence is huge and reach about 30%, what several times exceeds the numerical calculation accuracy. The bulk modulus counting accuracy of the mixed compounds concern is practically invariable.

Conclusions

From all the used exchange-correlation potential approximations E_{XC}, the best calculation results in terms of short and long range structures of mixed uranium and thorium dioxides enables the potential LSDA+U. However, what concerns the cohesive properties, the best results are obtained when the PBE-GGA+U potential is used.

Density functional theory (DFT) calculations confirmed the experimental results that the lattice constants in the $Th_{1-x}U_xO_2$ compound decrease linearly with increasing mole ratio x what means that the uranium dioxide lattice constants are smaller than the thorium dioxide lattice constants. This leads to the conclusion that the uranium dioxide and thorium dioxide-based fuel pellets can be in different proportions and alternately located in the fuel rod because U-233 increase in the thorium pellet causes a decrease its volume what, in turn do not generate stresses between the rod clad and the pellet.

Information of short range structure of the mixed compound $Th_{1-x}U_xO_2$ was gained, particularly the real uranium-oxygen and thorium-oxygen distances, while the experimental data describe the averaged values of whole crystal. It was proved that uranium and oxygen atoms are moved along the direction (111), so that uranium-oxygen distances are smaller than thorium-oxygen distances and their values are, in first approximation, such as in pure UO_2 and ThO_2, respectively.

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Fig. 7. Interatomic distances U-O and Th-O vs. mole ratio x for $Th_{1-x}U_xO_2$ unit cell (LSDA+U).

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