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Density functional theory calculations of the water interactions with ZrO₂ nanoparticles Y₂O₃ doped

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Abstract. Development of a new electricity generation techniques is one of the most relevant tasks, especially nowadays under conditions of extreme growth in energy consumption. The exothermic heterogeneous electrochemical energy conversion to the electric energy through interaction of the ZrO₂ based nanopowder system with atmospheric moisture is one of the ways of electric energy obtaining. The questions of conversion into the electric form of the energy of water molecules adsorption in 3 mol% Y₂O₃ doped ZrO₂ nanopowder systems were investigated using the density functional theory calculations. The density functional theory calculations has been realized as in the Kohn-Sham formulation, where the exchange-correlation potential is approximated by a functional of the electronic density. The electronic density, total energy and band structure calculations are carried out using the all-electron, full potential, linear augmented plane wave method of the electronic density and related approximations, i.e. the local density, the generalized gradient and their hybrid approximations.

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1. Introduction

The water is well known conventional source of electrical energy used by mankind. In liquid state, it is traditionally used for the electric energy conversion by an external thermostat of hydropower plants. However, direct conversion of water in gas state, (atmospheric moisture) to electric energy, remained unrealizable for centuries as a top scientific and practical aim. With the development of nanotechnology, the implementation of these ideas becomes potentially possible. In this regard, a nanopowder system based on zirconia dioxide (ZrO_2) is the best candidate for the direct conversion of the energy of water adsorption into electric energy [1]. It is well known [1-2] that the ZrO_2 surface is an extremely nonequilibrium thermodynamically, the surface of the ZrO_2 based nano-dispersed oxide systems is exist in a state of dynamic charge and adsorption equilibration. I.e., the change of quantity of adsorbates is accompanied by a changing of the total charge in the system. In the case of nanoscale powder of zirconia dioxide, on its surface are preferably water is absorbed, and certain stages of a matter exchange between the system and external environment have an exothermic behaviour. Hence, in a cyclic mode, the nanopowder system based on ZrO_2 can convert the chemical energy of water molecules adsorption to an electric form [1-4].

As is known, traditional photoelectric converters use light energy to localize the electron-hole pair in the material of the so-called adsorber (Figure 1). Then the electron-hole pair is converted into a pair of free charge carriers by the heterojunction field.

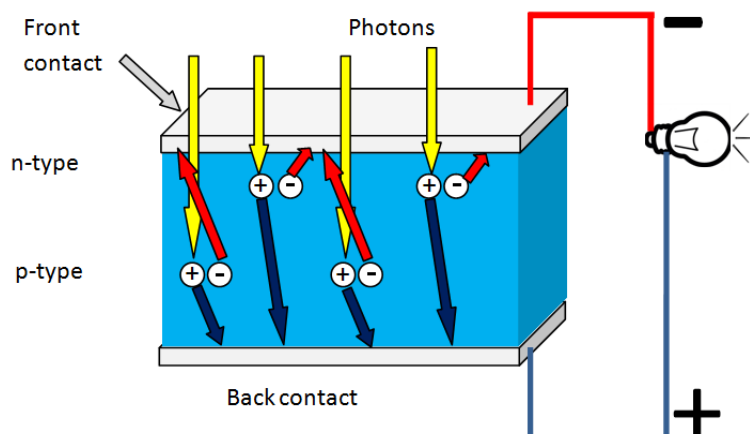


Figure 1. Schematic diagram of the operation of a traditional solar photocell (FEP).

To obtain such a heterojunction, some amount of impurity, with a valence greater than the valence of the base material (intrinsic semiconductor), for example, phosphorus, is introduced into the top layer of silicon. As a result, a layer is formed with an excess of electrons, that is, a negative charge. At the same time, the lower layer is doped with another valence impurity with a valence less than the valence of the intrinsic semiconductor, for example, by boron, which leads to a decrease in the number of electrons, thus creating a positive charge. As a result, an electric field is formed at the junction of these semiconductors, which provides separation and transport of free charge carriers to the electrodes.

The method of obtaining the energy considered in this paper is the phenomenon of injection of hot electrons (the mechanism of transfer of electric energy to the semiconductor crystal, which is realized during the course of a heterogeneous catalytic chemical reaction on its metalized surface) [5] (Figure 2). With a nanometer film thickness of <20 nm, so-called "hot electrons" with an energy of 1-3 eV ballistically, i.e. without loss of energy, reach the Schottky barrier and overcome due to its kinetic energy and, entering the semiconductor, form an electric current in the external circuit. Thus, in this case the appearance of free charge carriers is a consequence not of localization from the lattice, but of tunneling through the heterophase boundary to the outer space.

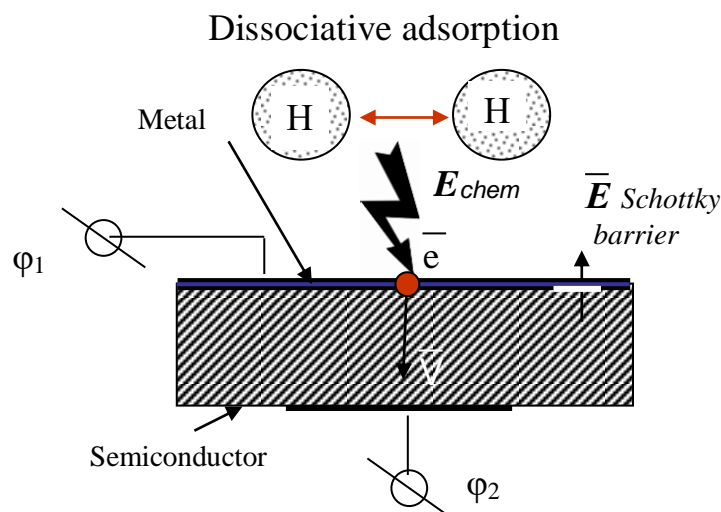


Figure 2. Scheme for the realization of the mechanism of ballistic electron transport on a metal-semiconductor transition during chemical adsorption.

The phenomenon of energy conversion of heterogeneous exothermic chemical reactions by analogy with photo-EMF [3] was called chemo-EMF (the prefix of chemo-, like photo-, emphasizes the nonthermic origin of the phenomenon) [6-9]. This way of converting chemical energy into an electrical form is good because the transformation from the chemical form of energy into electrical energy occurs directly, bypassing the intermediate stages.

There are other ways of obtaining electrical energy from moisture. For example, attempts have been made to collect a charge from jumping droplets of water mist by means of electrostatic capture or causing mechanical vibrations of piezoelectric plates [10-11]. These methods of obtaining energy assume the presence of intermediate energy forms and will have a lower efficiency than in the case of direct energy conversion. However, until now it is not clear in which act of a physico-chemical process a free electron is formed. It can be assumed that when a surface of a nanoparticle interacts with a water molecule, a process similar to that realized in redox processes takes place [12]. This paper is based on the results of the DFT calculations of the structure and energy state of the surface layer of nanoparticles of a solid solution based on ZrO₂ [13]. The main tasks of work are:

1. To calculate the energy characteristics of the system, to predict the most probable path of realization of oxidation-reduction processes on the surface of nanoparticles of the investigated disperse system,
2. Calculate the oxidation-reduction potentials of the system,
3. To determine the reaction pathway,
4. To find the EMF of the reaction, and the energy that can be produced when the electron formed by the interaction of the water molecule with the surface of ZrO₂ - nanoparticles, at $E_{V-/V} = 0.7V$; $E_{OH/OH} = 0.3V$, $\Delta E = EMF = 0.4V$. To check the scheme 1 realization. To calculate the allocated energy $W = -e \Delta E$ [14].

1.1. The nature of the adsorption of gas molecules by the surface of nanoparticles of oxides.

Theoretically, any oxide nanoparticle is a spherical fragment 4-10 nm in diameter, isolated from a regular crystal lattice of an ionic crystal. According to the principle of electroneutrality, the surface of such a nanoparticle is initially electrically neutral, a violation of the periodicity of the crystal potential by the surface leads to the formation of additional eigen levels in the forbidden gap of the energy spectrum of the crystal. These are the so-called Shockley / Tamm localized states, which can be treated as unsaturated chemical bonds of atoms on the surface [15-17]. In the chemical sense, these are the so-called "active centers". Depending on whether the levels are donor or acceptor, the nature of the

adsorbed ions will depend and, subsequently, the sign of the surface charge of the particle. In [18], it was proposed to use the value of its isoelectric point: pE as an index of the chemical activity of oxides.

Coordinative, the unsaturated surface Zr^{4+} cations are strong acid sites of adsorption (Lewis centers, $pE < 7$), therefore, the localized states in ZrO_2 are of a donor nature. Thus, the influx of neutral molecules into the reaction zone (the region near the surface of the nanoparticles) is provided due to the individual chemical properties of the nanoparticle material and its defectiveness.

The density functional theory (DFT) calculations aimed on determining the nature of the active centers responsible for the formation of a free charge carrier in the system under study. In DFT modeling we simulate water adsorption mechanism on the surface of nanosized yttria-stabilized zirconia (YSZ) (Figure 3). For the DFT calculations we have been aimed to perform a comparative analysis of water molecule interaction with two different surfaces:

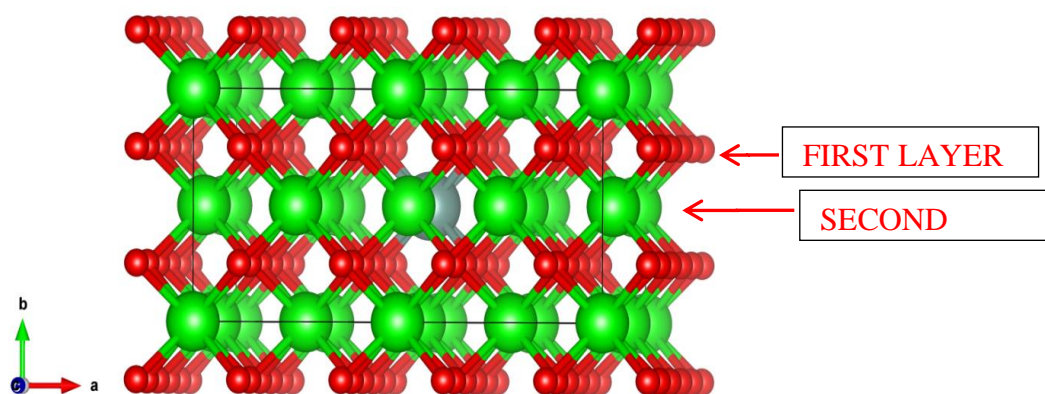


Figure 3. (Color online) A model structure of the ZrO_2 system doped with Y_2O_3 . The structure model ($ZrO_2 + 3\% \text{ mol } Y_2O_3$) includes 15 atoms of Zr, 32 atoms O and one atom of Y. The zirconium atoms are shown in green, oxygen atoms - in red, yttrium atom - in cyan. All calculation of charge density were performed for top layers.

(1) ZrO_2 and (2) $ZrO_2 + 3\% \text{ mol } Y_2O_3$

Below the electronic structure calculations present the electronic densities, energy bands, densities of states (DOS), X-ray spectra separately for ZrO_2 and $ZrO_2 + 3\% \text{ mol } Y_2O_3$ models. Next, the DFT calculated results are compared respectively for the systems:

(3) H_2O / ZrO_2 and (4) $H_2O / ZrO_2 + 3\% \text{ mol } Y_2O_3$.

So far, the developing of computational DFT technique for the above listed molecular systems has aimed on the accurate description of their electronic structures. As one expect, the replacing of zirconium with yttrium causes a large shift in the energy gap, making the compound $ZrO_2 + 3\% \text{ mol } Y_2O_3$ a more active target for the water absorption.

1.2. The DFT technique

The density functional theory (DFT) in the Kohn-Sham formulation [19] and its practical utilization by different approaches [20] is the most widely used approach for today electronic states calculations of functional materials. In the DFT method the exchange-correlation potential is approximated by a functional of the electronic density; the most common approximations are the local density approximation (LDA) [20], the generalized gradient approximation (GGA) [21], and the hybrid approximation [22]. One have to mention some peculiarities here, that while LDA and GGA provide a successful description of ground-state properties in crystals, this success does not extend to a

description of excited states. In many systems (semiconductors, crystal lattices, etc) the LDA and GGA strongly underestimate the value of the energy gap. Improved values for the band gaps are usually obtained by using the GW method [23]. However, the high computational cost of this method limits its applicability to crystals with a small number of atoms in the unit cell. An exchange potential was recently proposed by Becke and Johnson (BJ), designed to yield the exact exchange potential in atoms [24]. Unfortunately, the use of this potential led to a slight improvement in the energy gap values for many semiconductors [25]. A simple modification of the BJ potential was proposed by Tran and Blaha (TB-mBJ method). Studies have shown that the TB-mBJ potential is generally as accurate in predicting the energy gaps of many semiconductors as the much more expensive GW method [26].

In the present work, the total energy and band structure calculations are carried out using the all-electron, full potential, linear augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code [27]. We have utilized the WIEN2k code calculations for the 3 mol% Y_2O_3 doped ZrO_2 interacting with H_2O . Thereby, in the DFT/WIEN2k each atom is surrounded by a muffin-tin sphere, and the total space is divided into two regions. One region consists of the interior of these non-overlapping spheres, while the rest of the space constitutes the interstitial region. The radii of the muffin-tin spheres are $2.1a_0$ for Zr, $1.9a_0$ for O, $2.1a_0$ for Y and $0.6a_0$ for H, where a_0 is the Bohr radius. In GGA calculations, the exchange correlation potential is that proposed in reference [21]. The valence electrons' wave functions inside the muffin-tin spheres are expanded in terms of spherical harmonics up to $l_{max}=10$. In the interstitial regions, they are expanded in terms of plane waves, with a wave vector cutoff of K_{max} . Because of the small muffin-tin radius of hydrogen atoms, we set $R_H K_{max}=1.12$ in ZrO_2 and $ZrO_2+3\%$ mol Y_2O_3 , where $R_H=0.32a_0$ is the muffin-tin radius of the H atom. In the remaining four compounds, we set $R_{mt} K_{max}=2.1$, where R_{mt} is the smallest muffin-tin radius. The charge density is Fourier expanded up to a maximum wave vector of G_{max} , where $G_{max}=12a_0^{-1}$ for ZrO_2 , $G=12a_0^{-1}$ for $ZrO_2+3\%$ mol Y_2O_3 , and $G=20a_0^{-1}$ for the remaining compounds. The convergence of the self consistent calculations is achieved with a total energy tolerance of 0.001mRy and a charge convergence of 0.0004e.

2. The results summary of native experiments

2.1. The mechanism of formation of free charge carriers during the adsorption of a neutral water molecule. The potential energy of the chemical interaction of atmospheric molecules with the surface of a solid base.

Proceeding from the principle of electroneutrality [28] we will consider the number of negative and positive ions in the atmosphere equal, and the atmosphere as a whole - electrically neutral. Let us consider the mechanism of inflow to the surface of a nanoparticle based on zirconia dioxide of neutral water molecules and the selection of the energy of chemical interaction.

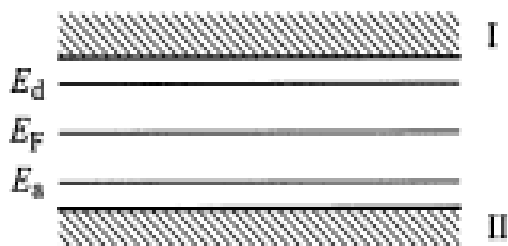


Figure 4. Qualitative band model of β - ZrO_2 with yttrium (a), with oxygen vacancies (b), with yttrium and oxygen vacancies (c).

I is the conduction band, and II is the valence band.

2.2. The nature of the adsorption of gas molecules by the surface of nanoparticles of oxides.

Theoretically, any oxide nanoparticle can be represented in the form of a spherical fragment with a diameter of 4-10 nm, isolated from a regular crystal lattice of an ionic crystal. According to the principle of electroneutrality, the surface of such a nanoparticle is initially electrically neutral.

2.3. The mechanism of charge compensation of an impurity in the system $ZrO_2 - Y_2O_3$.

In a solid substitution solution based on zirconium dioxide, the Y^{3+} impurity atoms have one electron less than the Zr^{4+} atoms and are acceptors, that is, they create in the forbidden band levels near the top of the valence band. The oxygen vacancies V_O are formed to compensate the excess volume and charge of the impurity are electron donors, ie, donor levels (holes, near the bottom of the conduction band Figure 4) are created near the bottom of the conduction band. The acceptor and donor character of β - ZrO_2 for Y^{3+} and oxygen vacancies, respectively, is confirmed by the results of [29]. As a result of thermal fluctuations, the holes give the electron to the conduction band (ionization of the hole), which by a Coulomb interaction finds an impurity atom and hits its orbital [30]. An impurity-vacancy dipole (IVD) of the Me- V_O type is formed, and the corresponding ionic bond according to [31] is the stabilizing element of the lattice (T-phase). In this case, the impurity atom acquires a negative charge $Y^{3+(-)}$, and the vacancy is a positive $V^{(+)}$. That is, donors and acceptors co-exist in the form of $V^{(+)} - Y^{3+(-)}$ IVD type²

2.4. The formation of an adsorption layer on the surface of particles. An own localized electronic states.

Violation of the periodicity of the crystalline potential by the surface (breaking of chemical bonds) leads to the formation of eigen levels in the band gap of the energy spectrum of the crystal-Shockley/Tamm localized states, which can be treated as unsaturated chemical bonds of atoms on the surface [32]. Their concentration in the ideal case should be equal in order of magnitude to the concentration of surface atoms. Such a configuration of the surface is not energetically favorable, so the population of these states (saturation of free valence bonds) occurs mainly by adsorption of molecules and ions from the atmosphere by the surface of nanoparticles. Thus, the influx of neutral molecules into the reaction zone (the region near the surface of the nanoparticles) is provided by the individual chemical properties of the nanoparticle material and its defectiveness.

2.5. Adsorption of molecules from the gas phase in $ZrO_2 - 3 \text{ mol\% } Y_2O_3$.

If the level is acceptor, on it with a probability determined by the Fermi-Dirac function

$$f = \left[1 + \exp\left(\frac{E_f - E_c}{kT}\right) \right]^{-1} \quad (1)$$

The electron (belonging to the nanoparticle material) is localized, additional surface states are filled at the bottom of the conduction band, and the bond formation between the surface and adsorbates is formed by the exchange interaction. As a result, a potential-forming layer of adsorption origin is formed (Helmholtz layer [33, 34], 2, Figure 5), and the neutral surface acquires a charge. In the case of $ZrO_2 - 3 \text{ mol\% } Y_2O_3$, this charge is negative. To compensate the charge of the potential-forming layer, an external diffuse layer is formed (3, Figure 5).

2.6. The structure of the reaction zone.

A particle of a dispersed phase, together with a DEL, is called a micelle (Figure 5). The aggregate of the substance $\{[ZrO_2] m\}$ with potential-forming ions, (predominantly OH^- for $ZrO_2 + 3 \text{ mol\% } Y_2O_3$ [35, 36]) form the core of the micelle $\{m [ZrO_2] nOH^-\}$. Potential-forming ions are connected with the surface of a relatively strong ($E > 0.3 \text{ eV}$ [37]) chemical bond. The diffuse layer is connected with the core of the micelle physically by the forces of electrostatic interaction and consists mainly of H^+

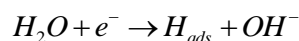
² The nanoparticle as a physical object can be considered theoretically as a nano-sized fragment of an extended electrically neutral crystal lattice of a solid solution of the appropriate composition. Consequently, initially the nanoparticle is electrically neutral.

protons and polarized water molecules. It is the diffuse layer that is the receptor of molecules from the outer atmosphere and their supplier into the reaction zone. The system of adsorbates on the surface of ZrO_2 is in dynamic equilibrium [38]. Consequently, when the external conditions change, it undergoes a change and a charge state of the near-surface layer.

The real mechanism of interaction of the water molecule with the surface of the micelle is multistage and is theoretically considered in detail in [39-40]. An interesting question is how the adsorption energy is transferred from the diffuse layer to the heterophase boundary, that is, to the surface of the nanoparticles.

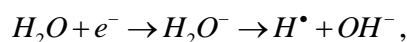
2.7. The physical basis of the chemoelectronic effect.

Upon reaching the surface of an electrically neutral zirconium oxide nanoparticle, the neutral water molecule under dissociation of the surface force gradient dissociates into a proton of the H^+ and OH^- group. In the case of physical adsorption, an electrochemical process is realized such as [41]:



The total charge of the surface changes, in this case, becomes negative. This leads to bending of the levels in the energy bands, and the charge exchange of electronic states localized near the surface. In particular, the localization of a part of electrons from the crystal lattice of nanoparticles near the surface and the formation of a space-charge region of an electronic type occur there with the probability determined by the Fermi-Dirac function. This region can be used as electrical capacitance in the development of ionistors.

In the case of chemical adsorption, processes with electron transfer via the phase interface are probably realized. Taking into account the acceptor character of the impurity level in the system under study, it can be assumed that the process proceeds according to the scheme [42]:



where H^\bullet – a radical hydrogen form.

Schematic representation of the proposed process is shown in Figure 6. The formation of a radical form of hydrogen leads to the launch of a chain reaction of ionization of the molecules of the dispersion medium. As a result, by the relay mechanism the charge is transported to the region with a lower charge concentration of the corresponding sign.

Unlike photocatalytic systems, the nanopowder heterophase system is thermodynamically closed, i.e., does not receive energy from outside as radiation, and as a consequence has a specific physical limit on electron production.

3. Simulation results

3.1. ZrO_2 : crystal and energy bands structures.

The cubic unit cell with space group $Fm\bar{3}m$ and lattice constants $a=b=c=4.938 \text{ \AA}$ was used in DFT calculation. The lattice parameters obtained (Table 1.) show excellent agreement with the experimental results and the differences is less than 3%. The calculated surface energies are presented in Table 2, which the minimum lattice energy in the 120.13 \AA^3 is received -165.2 eV. This volume of unit cell was chosen to all calculation experiential. Calculations were performed using Abinit code and GGA (PBE) - Fritz-Haber-Institute (FHI) pseudopotential with energy convergence of 0.0001.

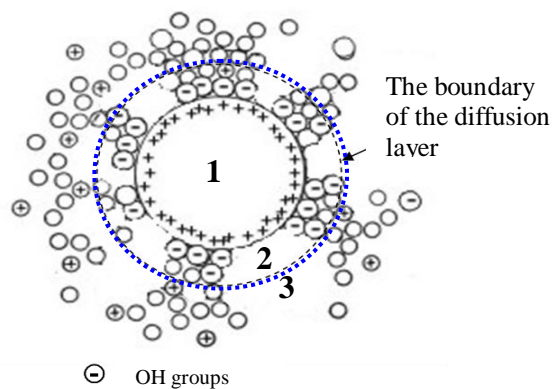


Figure 5. Schematic representation of a ZrO_2 (1) nanoparticle surrounded by an ionic atmosphere, including adsorption (2) and diffuse (3) layers.

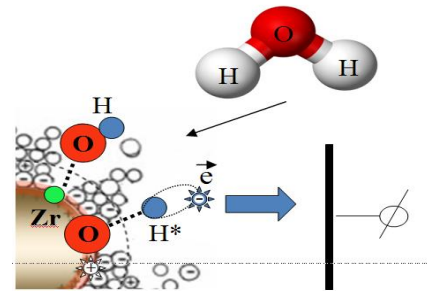


Figure 6. Schematic representation of a possible electrochemical process with an electron transfer through the phase-gap interface during adsorption of water molecules to the surface of nanoparticles based on ZrO_2 .

Table 1. Calculated and observed structural parameters of cubic ZrO_2 (a[43]; b[44]; c[45]).

Parameters	(exp)	(calc)
$a=b=c$ (Å)	4.913 ^a 5.07 ^b	4.938
Lattice energy per ZrO_2 (eV)	-109.76 ^c	-165.2
Lattice Energy per $\text{ZrO}_2+3\%$ mol Y_2O_3 (eV)	-106.1 ^c	141.2

Table 2. Lattice energy per unit cell for both ZrO_2 and $\text{ZrO}_2+3\%$ mol Y_2O_3 .

Lattice Energy per unit cell ZrO_2 (eV)	-138.6	-158.4	-163.1	-159.25	-165.2	-148.13	-84.1
Lattice Energy per unit cell $\text{ZrO}_2+3\%$ mol Y_2O_3 (eV)	-124.75	-137.88	-139.1	-137.25	-141.2	-132.75	-76.75
Volume Å ³	114.79	116.58	118.58	119.35	120.13	121.43	122.46

In Figure 7 we present the calculated energy bands of ZrO_2 . The electronic density of states in Figure 7 have shown for high symmetry directions of the Brillouin zone (BZ). The valence band maximum (VBM) and conduction band minimum (CBM) occur at the Γ -point, the BZ center. In ZrO_2 , the gap occurs at point R(1/2, 1/2, 1/2). Point R of the cubic lattice BZ is zone-folded into the Γ -point of the body-centered tetragonal lattice BZ. The density of states of ZrO_2 is shown in Figures 8 (top and bottom), where we see that the low-lying conduction bands are derived from O p states. On the other hand, the bands in the range -2 eV to 0 eV are dominated by oxygen-derived states. The valence band just below the Fermi energy is derived from zirconium s and p states. These observations become clear upon considering the atomic orbital character of the bands, which is presented in Figure 8 (bottom). The contribution of the chosen atomic orbital to the eigenstates at each k -point, where the CBM is derived mostly from Zr p states. The VBM also dominated by Zr, though a mixture of Zr s and O p states is clear. The anti-bonding state formed from these s and p states is pushed up in energy close to the Fermi level. The large contribution of Zr s ($l = 0$) states to the VBM and Zr p ($l = 1$) states to the CBM suggests that there are some transitions between the VBM and CBM ($\Delta l = 1$), to be useful of this material in charge conduction process.

3.2. $ZrO_2 + 3\% \text{ mol } Y_2O_3$: crystal and energy bands structures.

A model structure of the zirconium dioxide doped with yttrium is shown in Figure 9. The structure model ($ZrO_2 + 3\% \text{ mol } Y_2O_3$) includes 15 atoms of Zr, 32 atoms O and one atom of Y. The zirconium atoms are shown in green, oxygen atoms - in red, yttrium atom - in cyan. All calculation of charge density were performed for top layers as shown in Figure 3 above.

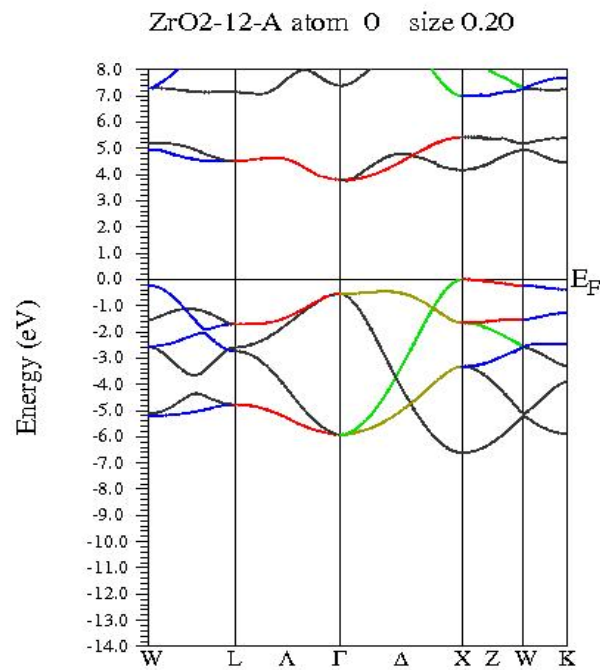
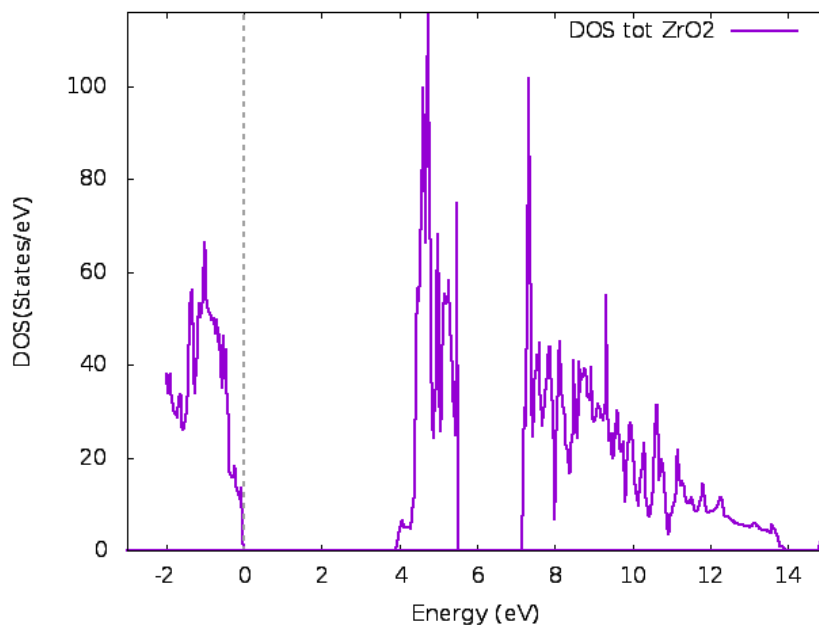


Figure 7. The calculated energy bands of ZrO_2 .



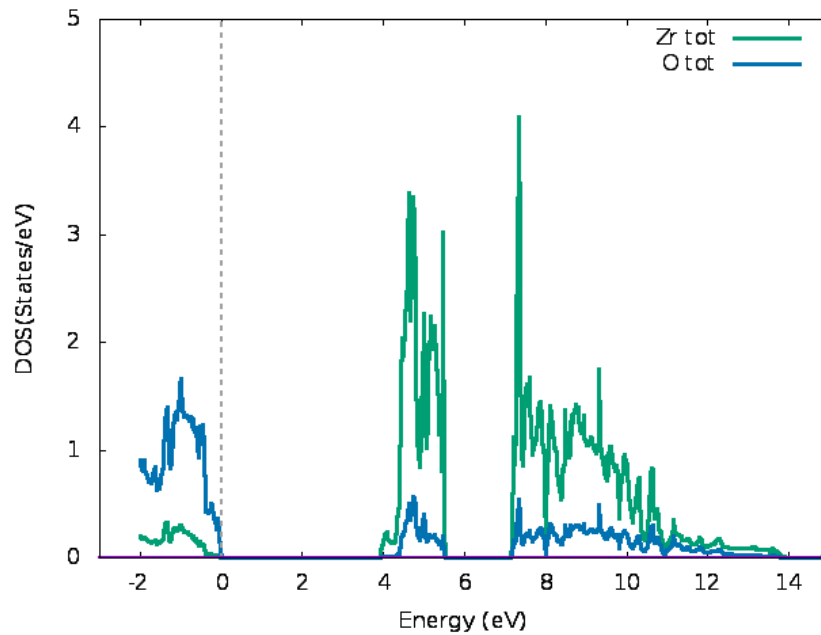


Figure 8. The calculated densities of states of ZrO_2 (top and bottom).

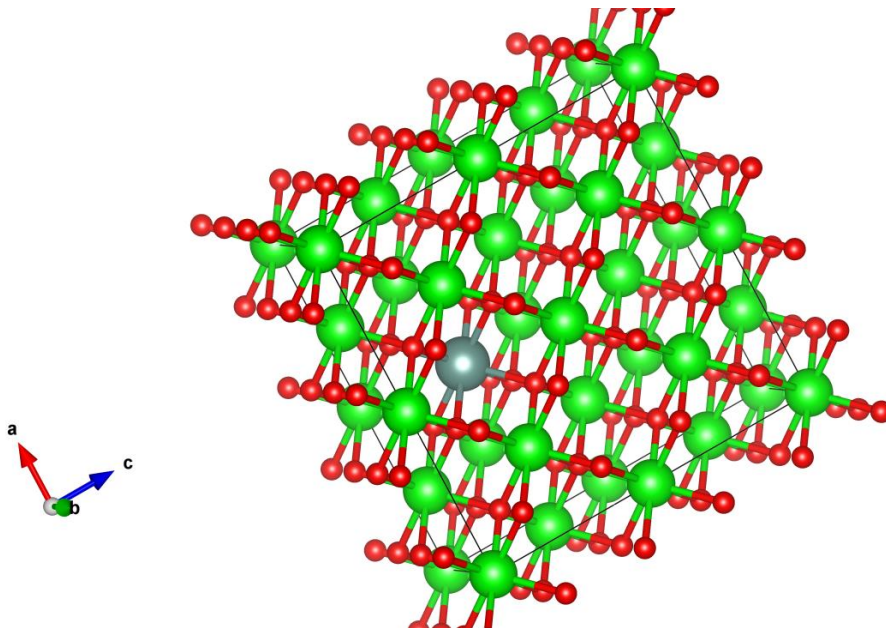


Figure 9. (Color online) A model structure of the ZrO_2 system doped with Y_2O_3 . The zirconium atoms are shown in green, oxygen atoms - in red, yttrium atom - in cyan.

In Figure 10 the calculated energy bands are presented for the system $\text{ZrO}_2 + 3\% \text{ mol } \text{Y}_2\text{O}_3$. The electronic density of states in Figure 11 demonstrate the relatively higher densities, in comparison with ZrO_2 (Figure 7), and narrowing of the gap between the VBM and CBM zones. The Fermi level slightly shifted up to, so the gap between the VBM and CBM has narrowed on 1 eV.

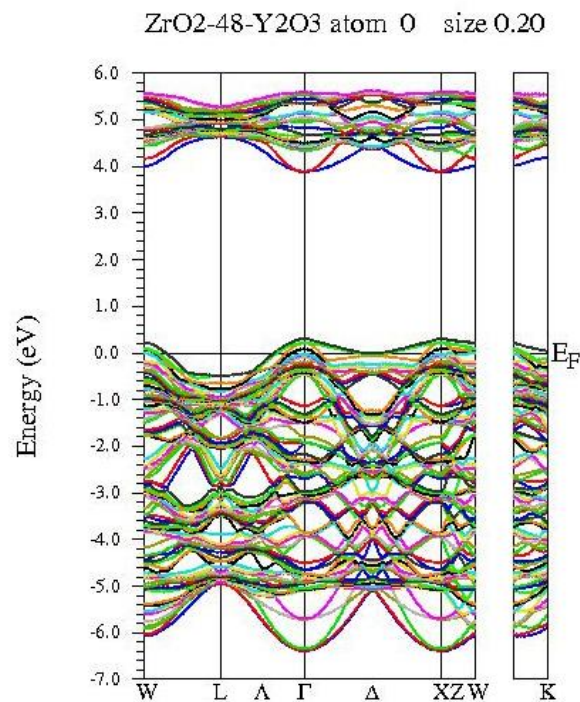
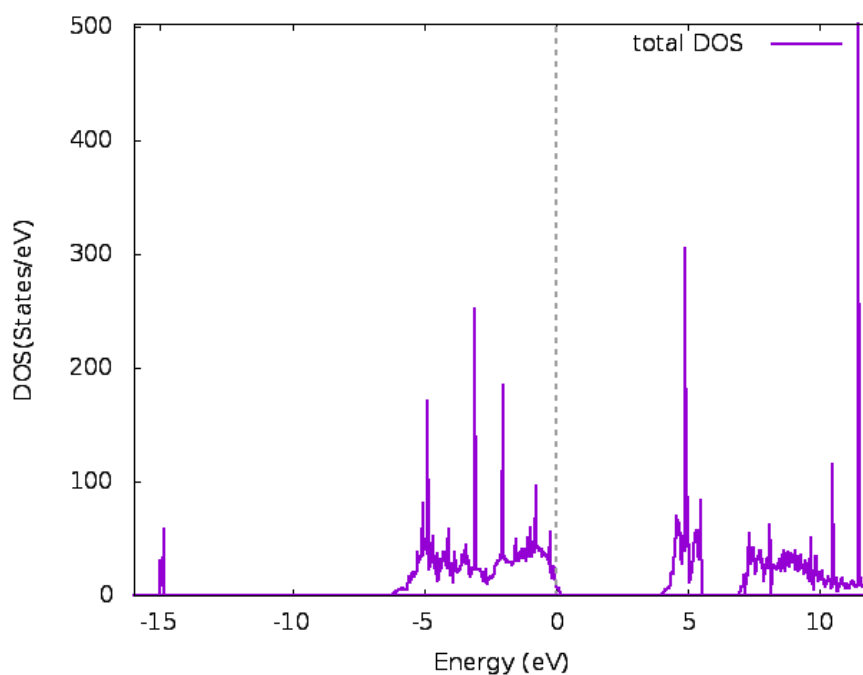


Figure 10. The calculated energy bands of ZrO₂+ 3% mol Y₂O₃.

Figures 11 (top and bottom) show the density of states for ZrO₂+ 3% mol Y₂O₃. Now doping of yttrium to the zirconia structure causes the dominating of oxygen in the interval from -5 eV to 0 eV. At the same time, the yttrium with zirconium dominate together in the conduction zone. These observations clearly demonstrate the atomic orbital modifications of the bands, which are influenced by the yttrium doping to the zirconium dioxide.



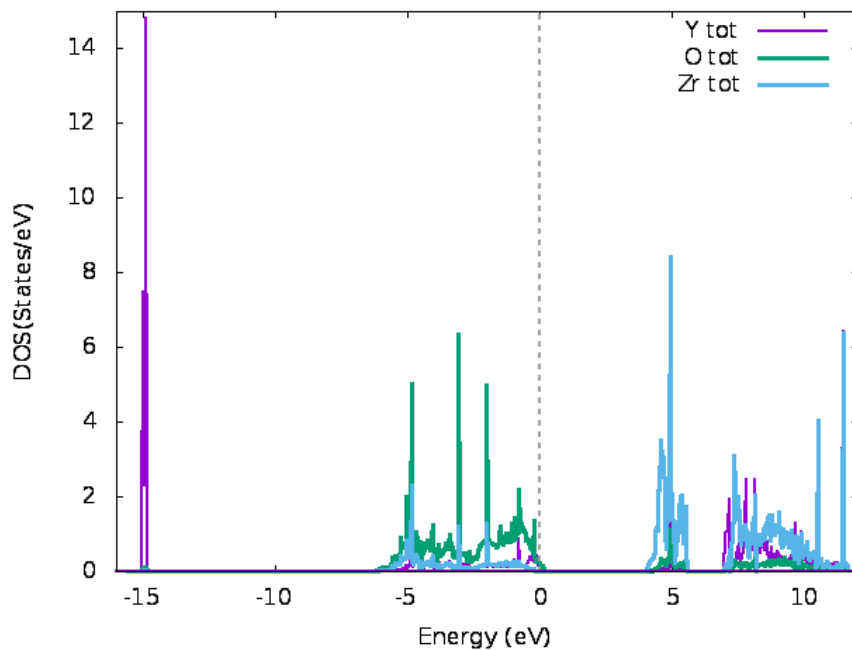


Figure 11. The calculated densities of states of $\text{ZrO}_2 + 3\% \text{ mol Y}_2\text{O}_3$ (top and bottom).

The calculated above electronic densities of $\text{ZrO}_2 + 3\% \text{ mol Y}_2\text{O}_3$ should be compared with the ZrO_2 model. We can observe the DOS spectra peculiarities for $\text{ZrO}_2 + 3\% \text{ mol Y}_2\text{O}_3$ that possess visibly higher amplitudes in comparison with ZrO_2 ones. This observation could be a precursor for a charge re-distribution process, anticipating a charge conduction of agents as like as water molecule on the $\text{ZrO}_2 + 3\% \text{ mol Y}_2\text{O}_3$ surface.

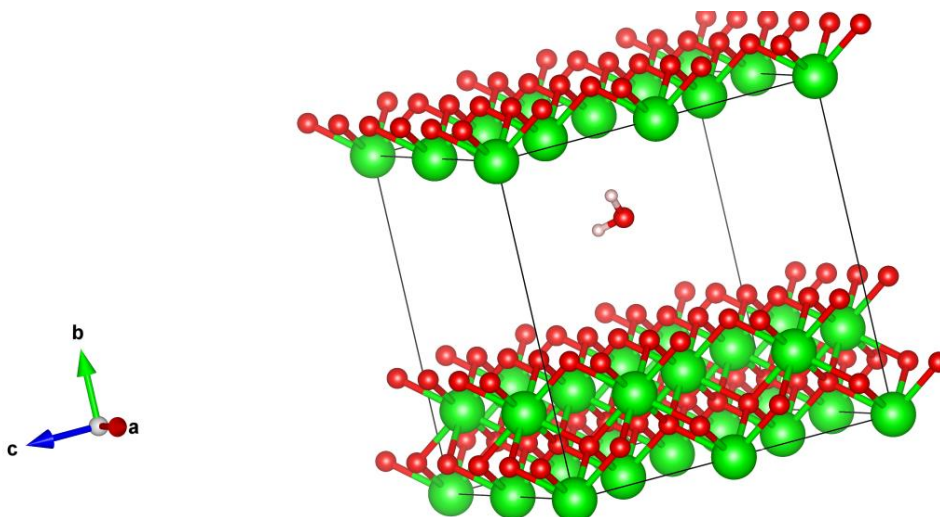


Figure 12. (Color online) A model structure of the $\text{H}_2\text{O}/\text{ZrO}_2$. The structure model ($\text{ZrO}_2 + \text{H}_2\text{O}$) includes 16 atoms of Zr and 32 atoms O of the periodic surface, and one water molecule. The zirconium atoms are shown in green, oxygen atoms - in red, hydrogen atom - in white. The distance between atom of oxygen of H_2O and first layer is 6.334199 Bohr.

3.3. H_2O/ZrO_2 – system.

So far, the use of DFT for the above listed molecular systems has aimed on the accurate description of their comparative electronic structures. As one expect, the replacing of zirconium with yttrium causes a large shift in the energy gap, making the compound $ZrO_2 + 3\%$ mol Y_2O_3 a more active target for the water absorption. Next, the DFT calculated results are compared respectively for the systems: (3) H_2O / ZrO_2 (Figure 12) and (4) $H_2O / ZrO_2 + 3\%$ mol Y_2O_3 (Figure 14).

In Figures 12-13 and 14-15 the configuration snapshots and calculated DOS are shown for H_2O/ZrO_2 and $H_2O/ZrO_2 + 3\%$ mol Y_2O_3 , respectively. The important observation is that the inducing 3% mol Y_2O_3 doping to system H_2O/ZrO_2 brought to the shift of DOS amplitude from 4 eV to 0. This is obviously indicate on a charge redistribution of the water interaction with zirconia surface as a result of ittrium ion doping.

Concluding the DFT results with the experimental data, it is worth noting that the idea is that, when molecule of water approaching on the surface of ZrO_2 ($ZrO_2 + 3\%$ mol Y_2O_3) it's kinetic energy leads to a change the DOS and the electron density of the ZrO_2 ($ZrO_2 + 3\%$ mol Y_2O_3). On the basis of the first Hohenberg and Kohn theorem the total energy calculated with this density of a electron system $\rho(r)$ will always be larger or equal then the ground state energy E_0

$$E_0 \leq E[\rho(r)] \quad (2)$$

At the kinetic energy transition of the water molecule T to above system (ZrO_2) according the first Hohenberg theorem the electron density of the system should be changed:

$$E_0 + T \leq E[\rho(r) + \Delta\rho(r)] \quad (3)$$

Depending on the distance between water molecule and first layer of ZrO_2 ($ZrO_2 + 3\%$ mol Y_2O_3) the kinetic energy transition will be different. Hence, in this simulation the distances between the water molecules and the oxide surface was chosen for the 4 values.

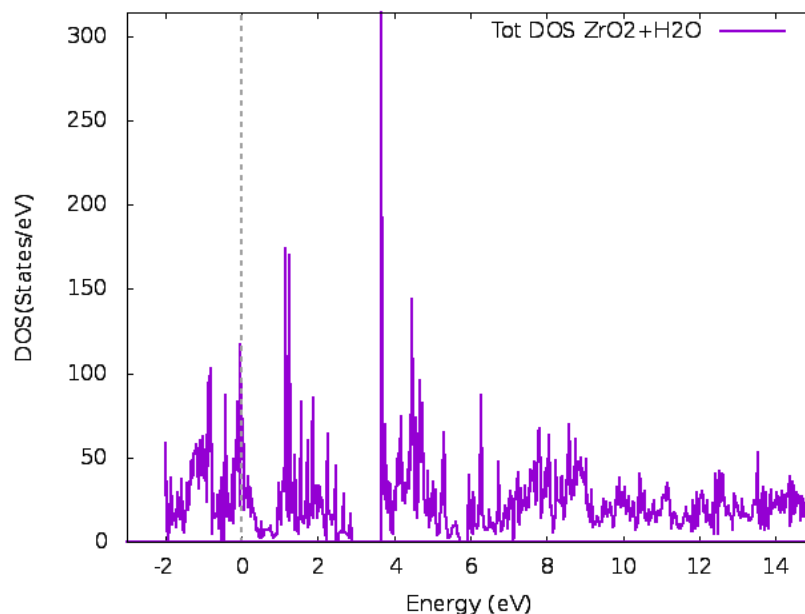


Figure 13. The calculated densities of states of H_2O/ZrO_2 (top, middle and bottom). The distance between atom of oxygen of H_2O and first layer is 2.6205095 Bohr.

3.4. $H_2O/ZrO_2 + 3\% \text{ mol } Y_2O_3$ - system

Concluding the DFT results with the experimental data, it is worth noting that the idea is that, when molecule of water approaching on the surface of ZrO_2 ($ZrO_2 + 3\% \text{ mol } Y_2O_3$) leads to a

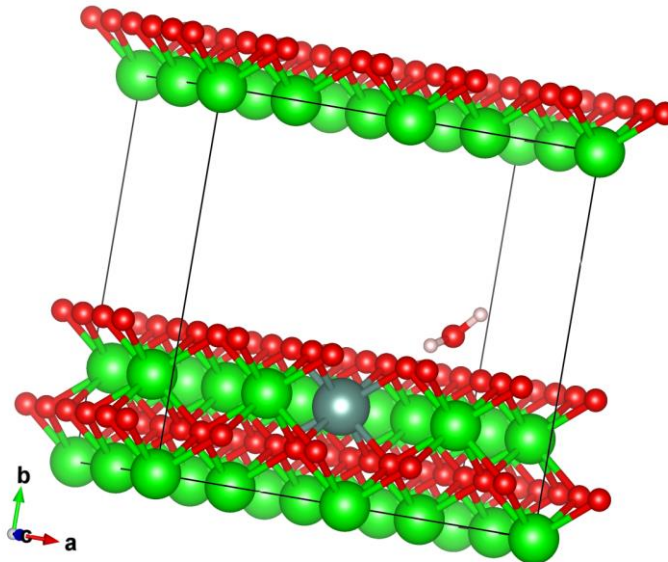


Figure 14. (Color online) A model structure of the $H_2O/ZrO_2 + 3\% \text{ mol } Y_2O_3$. The structure model ($H_2O/ZrO_2 + 3\% \text{ mol } Y_2O_3$) includes 15 atoms of Zr, 1 atom Y and 32 atoms O of the periodic surface, and one water molecule. The zirconium atoms are shown in green, oxygen atoms - in red, hydrogen atom - in white and yttrium atom - in cyan. The distance between atom of oxygen of H_2O and first layer is 1.32077 Bohr.

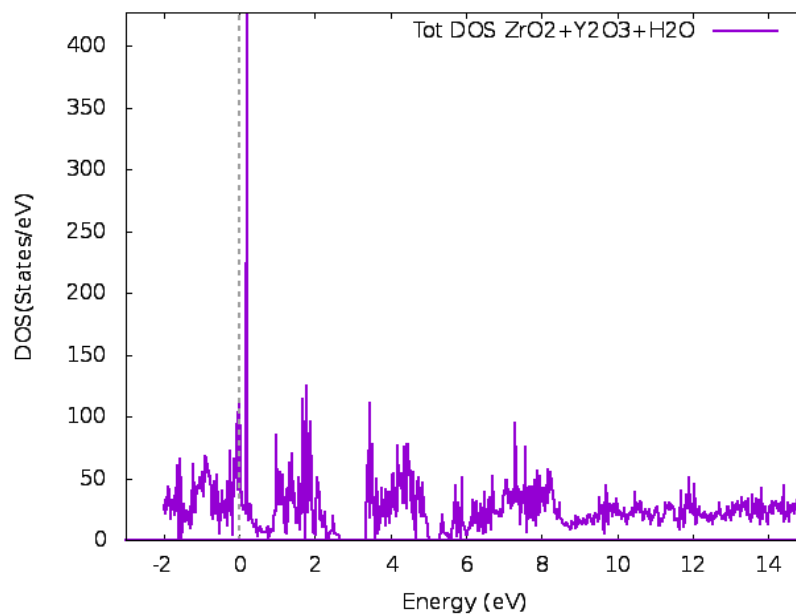


Figure 15. The calculated densities of states of $H_2O/ZrO_2 + 3\% \text{ mol } Y_2O_3$ (top and bottom). The distance between atom of oxygen of H_2O and first layer is 2.6205095 Bohr.

change the DOS and the electron density of the ZrO_2 ($\text{ZrO}_2+3\%$ mol Y_2O_3). On the basis of the first Hohenberg and Kohn theorem [46] the total energy calculated with this density of a electron system $\rho(r)$ will always be larger or equal then the ground state energy $E_0, E_0 \leq E[\rho(r)]$, At the kinetic energy transition of the water molecule T to above system (ZrO_2) according the first Hohenberg theorem the electron density of the system should be changed: $E_0 + T \leq E[\rho(r) + \Delta\rho(r)]$. Depending on the distance between water molecule and first layer of ZrO_2 ($\text{ZrO}_2+3\%$ mol Y_2O_3) the kinetic energy transition will be different. Hence, in this simulation the distances between the water molecules and the oxide surface was chosen for the 4 values.

4. Conclusions

Density functional theory calculations have been performed on ZrO_2 nanoparticles doped with Y_2O_3 and interacting with the water molecule to evaluate the electronic density, total energy and band structures. It is shown that the surface of ZrO_2 nanoparticles can be considered as a reaction zone for electrochemical processes.

The important observation is that the inducing 3% mol Y_2O_3 doping to system $\text{H}_2\text{O}/\text{ZrO}_2$ brought to the shift of DOS amplitude from 4 eV to 0. It's show's that water molecules adsorbed from the atmosphere on the surface of ZrO_2 -based nanoparticles leads to realization of the process of electron localization from the crystal lattice of nanoparticles and its transport outside the particles.

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