The role of oxygen vacancies on the structure and the density of states of iron doped zirconia.

Davide Sangalli,1 Alessio Lamperti,1 Elena Cianci,1 Roberta Ciprian,1 Michele Perego,1 and Alberto Debernardi1

1Laboratorio MDM - IMM - CNR via C. Olivetti, 2 I-20864 Agrate Brianza (MB) Italy

(Dated: May 1, 2014)

Abstract

In this paper we study, both with theoretical and experimental approach, the effect of iron doping in zirconia. Combining density functional theory (DFT) simulations with the experimental characterization of thin films, we show that iron is in the Fe\(^{3+}\) oxidation state and accordingly that the films are rich in oxygen vacancies (V\(_O^{••}\)). V\(_O^{••}\) favor the formation of the tetragonal phase in doped zirconia (ZrO\(_2\):Fe) and affect the density of state at the Fermi level as well as the local magnetization of Fe atoms. We also show that the Fe(2p) and Fe(3p) energy levels can be used as a marker for the presence of vacancies in the doped system. In particular the computed position of the Fe(3p) peak is strongly sensitive to the V\(_O^{••}\) to Fe atoms ratio. A comparison of the theoretical and experimental Fe(3p) peak position suggests that in our films this ratio is close to 0.5.

Besides the interest in the material by itself, ZrO\(_2\):Fe constitutes a test case for the application of DFT on transition metals embedded in oxides. In ZrO\(_2\):Fe the inclusion of the Hubbard U correction significantly changes the electronic properties of the system. However the inclusion of this correction, at least for the value U = 3.3 eV chosen in the present work, worsen the agreement with the measured photo-emission valence band spectra.

PACS numbers: 68.55.Ln, 71.15.Mb, 75.50.Pp
INTRODUCTION

In dilute magnetic semiconductors (DMS) magnetic impurities, usually transition metals (TM), are introduced to produce a magnetic ground state. These systems have been extensively investigated since the discovery of carrier induced ferro-magnetism in $(In, Mn)As$ and $(Ga, Mn)As$, and are believed to be fundamental to fabricate spin-based electronic devices. The understanding of DMS physical properties constitutes a challenge for the theory as the fundamental mechanism leading to ferromagnetic interaction can be hardly explained. Also experimentally the inclusion and the influence of TM doping is not clearly understood. Indeed, while several DMS were predicted to have a Curie temperature ($T_c$) above room temperature, no experimental report of $T_c > 300 K$ has been left unchallenged by other studies. Moreover some results suggest that magnetic impurities, at least at very low doping concentration, act as paramagnetic centers. Recently a new class of DMS, based on oxides such as zirconia ($ZrO_2$) and hafnia ($HfO_2$), has received great attention, after the experimental reports of room temperature magnetism in $Fe$ doped $HfO_2$ and $ZrO_2$ and the theoretical prediction of high $T_c$ in TM doped $ZrO_2$.

For a better understanding of the magnetic properties of the system, a clear picture of its structural and electronic properties is fundamental. As opposite to standard bulk materials, where usually the most stable configuration can be unequivocally identified, in DMS the inclusion of the dopant can induce stress, disorder and defects in the system with many possible configurations close in energy. From one side, theoretically, the modeling of the material, also at the first-principles levels, requires some assumptions on the initial structure and on the position occupied by the dopant. From the other side, experimentally, stress, disorder and defects make difficult to provide a unique interpretation to the features observed. Thus a combined approach is the best option.

Among the structural defects of dilute magnetic oxides (DMO), oxygen vacancies ($V_{O}^{••}$) are believed to affect the magnetism. Indeed it has been suggested that delocalized electrons, associated with $V_{O}^{••}$, can play a crucial role in the magnetization mechanisms of DMO. However, in this model, $V_{O}^{••}$ are assumed to always induce delocalized states, which can mediate the magnetic interaction. This assumption is true in the undoped oxide, while in presence of doping should be verified case by case.

In the present paper we describe the structural and electronic properties of iron doped
zirconia ($\text{ZrO}_2:Fe$) focusing our attention on the role of $V_O^{\bullet\bullet}$ and on their relation with the dopant. The role of $V_O^{\bullet\bullet}$ in $\text{ZrO}_2:Fe$, and more in general of $\text{ZrO}_2$ doped with valence +3 elements ($X^{+3}$, with $X = Fe, Y$, etc...) has been, in part, explored in view of different applications, for oxygen sensing and more recently for resistive switching memories. For $\text{ZrO}_2:Fe$ in particular only few experimental reports exist. Also for TM doped oxides in general, no systematic theoretical description of the relation between $V_O^{\bullet\bullet}$ and doping exist. For example the $V_O^{\bullet\bullet}$ formation energy, in presence of doping, is usually considered only for the $V_O^{\bullet\bullet}$ to dopant atoms ratio, $y_{V_O^{\bullet\bullet}}/X$, equal to 1 and again $V_O^{\bullet\bullet}$ are assumed to induce delocalized states which could mediate the electron conduction in case of resistive switching, regardless of the value of $y_{V_O^{\bullet\bullet}}/X$.

Instead, in case of $X^{+3}$ elements, like iron, the most stable configuration is expected to have $y_{V_O^{\bullet\bullet}}/X = 0.5$ for charge compensation. We thus focus our attention on this configuration describing how the properties of the system would change if $y_{V_O^{\bullet\bullet}}/X$ deviates from the value 0.5.

In sec. I we describe both the theoretical and the experimental approach to the description of $\text{ZrO}_2:Fe$. The results from first–principles simulations are presented in sec. II. The electronic and structural properties of the system are described in function of the doping and oxygen vacancies concentration within density functional theory (DFT) in the standard generalized gradient approximation (GGA). For TM oxides the standard approximations to DFT are known to fail in the description of the so called on–site correlation. Thus DFT can be corrected with a “Hubbard” term, DFT+$U$ scheme, where $U$ is an external parameter, which improves the DOS of the valence electrons. However little is known in the case of TM used as dopant in DMO. Thus we also investigate how this term would influence the electronic properties of the system in $\text{ZrO}_2:Fe$.

The experimental results are then presented in sec. III. Here we show that, indeed, the measured properties best agrees with the $y_{V_O^{\bullet\bullet}}/X = 0.5$ configuration. Moreover a detailed comparison of the measured valence band (VB) and DFT density of states (DOS) is done. This is a direct way to explore the value of the on–site electronic correlation on this system, i.e. to adjust the value of the $U$ parameter to be used in the DFT+$U$ approach.
I. FRAMEWORK

A. Computational approach

We computed, from first–principles, the ground state of the two most common phases of ZrO$_2$, i.e. the tetragonal and the monoclinic phases, at different doping concentrations. We used the PWscf (4.3.2) package$^{21}$, considering a super–cell with 96 atoms (few less when $V_O^{**}$ are considered) and in some cases also a smaller super–cell with 12 atoms for the description of the highest doping configuration. For all systems the atomic positions are fully relaxed. The ground state was computed within the GGA$^{22}$ to the DFT scheme$^{23,24}$ with ultra–soft pseudo–potentials$^{25,26}$. We used a 35 $Ry$ cut–off for the wave–functions, 400 $Ry$ cut–off for the augmentation density and a Monkhorst–Pack grid 2x2x2 for the Brillouin zone to have the error on the energy differences between the monoclinic and the tetragonal phase lower than 1 $meV$ per formula unit (f.u.); this was the most stringent condition for our simulations. We estimated the error on the total energy to be lower than 0.1 $eV/f.u$. Convergence parameters are $10^{-8}$ $Ry$ on the total energy for the scf cycles and both $10^{-4}$ $Ry$ on the total energy and $10^{-3}$ $Ry/Bohr$ on the forces for the atomic relaxation. The pseudo–potential of Zr includes semi–core electrons. $Fe$ atoms were placed at the substitutional Zr sites and kept as far as possible from each other to mimic uniform doping. For $V_O^{**}$ instead we considered many different configurations (see discussion in sec. II), specifically we considered ZrO$_2$:Fe at the atomic doping concentration $x_{Fe} = 6.25\%$, 12.5\%, 18.75\%, 25\% with, $y_{V_O^{**}/Fe} = 0.5$, and without, $y_{V_O^{**}/Fe} = 0$, oxygen vacancies. We also considered $y_{V_O^{**}/Fe} = 1.0$ for $x_{Fe} = 6.25\%$, 25\%. In total we studied about 50 different systems of Zr$_{1-x}Fe_xO_{2-z}V_O^{**}$ changing $x_{Fe}$ and $z_{V_O^{**}} = x_{Fe} \times y_{V_O^{**}/Fe}$ for either the monoclinic or the tetragonal structure. For few selected configurations, i.e. at the lowest and the highest considered doping concentrations $x_{Fe} = 6.25$, 25%, we also performed calculations within the simplified GGA+$U$ approach$^{44}$ implemented in the PWscf package, again considering $y_{V_O^{**}/Fe} = 0$, 0.5, 1, in order to explore the effect of the Hubbard correction on the electronic structure of the system. The results are presented mainly for the high–doping situation which we have also experimentally. The configurations at $y_{V_O^{**}/Fe} = 0$ and 1 resulted to be metallic and in these case the convergence of the physical quantities against the sampling of the k–points grid was verified.
The cell parameters for both the tetragonal and the monoclinic phase of pure ZrO$_2$ are the same used in Ref. 31. Specifically for the monoclinic phase $a = 5.18$ Å, $b/a = 1.011$, $c/a = 1.037$ and $\beta = 99^\circ10'$; while for the tetragonal phase $a = 5.18$ Å and $c/a = 1.0305$. The same parameters were used for ZrO$_2$:Fe as well. However we even performed a full relaxation of our 96 atoms super-cell for few selected configurations and we found out that this have a negligible impact on the properties of the system here considered.

In sec. II we systematically compare the results of the present simulations with the ZrO$_2$:Y (Y doped ZrO$_2$) system. Yttrium is one of the most studied and used dopant of ZrO$_2$ and shares with iron the same valence. All the data reported for ZrO$_2$:Y are from ref. 31.

In order to describe the semi–core levels of iron and compare the results with XPS measurements, we run calculations with a norm–conserving fully–relativistic approach. To this end, we used Hartwigsen, Goedecker, and Hutte (HGH) pseudo–potentials which contain semi–core electrons in valence and are constructed with a fully relativistic calculation. The latter are not available within the PWscf code and so we used the abinit (6.8) code. We studied the semi–core levels only for the $x_{Fe} = 25\%$ at. case again considering $\nu_{V^{**}O}/Fe = 0$, 0.5, 1. We used smaller super–cells, 12 atoms ($\nu_{V^{**}O}/Fe = 0$ and 1) and a 24 atoms supercell ($\nu_{V^{**}O}/Fe = 0.5$), with cut–off of 170 Ry and a Monkhorst–Pack grid 3x3x3 and 3x3x2 respectively for the Brillouin zone to have the error on the energy levels position lower then 0.1 eV. The very high energy cut–off was needed, as the norm conserving HGH pseudo–potentials are harder than the ultra–soft ones used with PWscf and also because the semi–core levels are much more localized than valence electrons. The value $x_{Fe} = 25\%$ at. was chosen to have smaller super-cells but also because this is quite close to the experimentally measured doping concentration in our films. The atomic positions instead were obtained relaxing the same structures with the PWscf code and then we checked that the residual forces on the atoms computed with Abinit were negligible.

Finally for a quantitative comparison of the measured photo–emission and the computed valence band we have performed calculations within GGA+$U$ at $U = 1.0$, 2.0, 3.3 eV at $x_{Fe} = 18.75\%$ at. and $\nu_{V^{**}O}/Fe = 0.5$. A theoretical smearing of 0.02 $Ry$ was used to generate the DOS used in Figs. 3-4 while a higher smearing of 0.06 $Ry$ was used for the DOS in Fig. 7 to mimic the experimental peak width.
B. Experimental setup

Experimentally $ZrO_2$ and $ZrO_2:Fe$ thin films were grown on $Si/SiO_2$ substrates in a flow–type hot wall atomic layer deposition reactor (ASM F120) starting from $\beta$–diketonates metalorganic precursors, namely $Zr(C_{11}H_{19}O_2)_4$ for $Zr$ and $Fe(C_{11}H_{19}O_2)_3$ for $Fe$. To grant a stable reactivity, $Zr$ precursor was kept at 170°C, while $Fe$ precursor was maintained at 115°C. Ozone was used as oxidizing gas in the reaction process. The film growth was achieved by alternately introducing the reactants separated by $N_2$ inert gas purging pulses. The $Fe$ concentration in $ZrO_2:Fe$ films was tuned tailoring the $Zr/Fe$ precursors pulsing ratio and the growth temperature was maintained at 350°C (details in Ref. 29). After the deposition the films were annealed at 600°C in $N_2$ flux for 60s. The growth parameters were tuned in order to fix the thickness, $d = 19 \pm 1 \, nm$, and the doping concentration $x_{Fe} = 20\% \pm 3\%$ for the $ZrO_2:Fe$ films. $x_{Fe}$ was chosen in order to stabilize the tetragonal phase according to our theoretical results.

Film crystallinity was checked by X–ray diffraction (XRD) at fixed grazing incidence angle $\omega = 1^\circ$ and using $Cu \ K_\alpha$ ($\lambda = 0.154 \, nm$) monochromated and collimated X–ray beam (details in Ref. 30). Film uniform doping along its thickness was checked by Time of Flight Secondary Ion Mass Spectrometry (ToF–SIMS) depth profiling using an ION–TOF IV instrument, with 500 eV $Cs^+$ ions for sputtering and 25 keV $Ga^+$ ions for analysis. Secondary ions were collected in negative polarity and interlaced mode. Recorded intensities were normalized to $^{30}Si$ intensity in bulk silicon. The instrument depth resolution is below 1 nanometer.

To elucidate $Fe$ chemical state and concentration in $ZrO_2:Fe$ films, X–ray photo–emission (XPS) measurements were performed on a PHI 5600 instrument equipped with a monochromatic Al $K_\alpha$ x-ray source ($E = 1486.6 \, eV$) and a concentric hemispherical analyzer. The spectra were collected at a take–off angle of $45^\circ$ and band–pass energy 11.50 $eV$. The instrument resolution is 0.5 $eV$.
II. FIRST PRINCIPLES PREDICTIONS

A. $V^\bullet\bullet_O$ and structural properties

In the literature $ZrO_2:Fe$ has been studied as a candidate material for oxygen sensing applications because $Fe^{+3}$ atoms, replacing $Zr^{+4}$ atoms, are expected to induce oxygen vacancies for charge compensation\textsuperscript{16,17}. Thus, as a first step, we consider the $V^\bullet\bullet_O$ formation energy:

$$\Delta E_1(x_{Fe}, z) = \left( E[Zr_{1-x}Fe_xO_2] - ( E[Zr_{1-x}Fe_xO_2-z] + (z/2)\mu[O_2] ) \right)/z$$

(1)

at fixed $y_{V^\bullet\bullet_O}/x = 0.5$, i.e. for a charge compensated system. Here we considered both the oxygen rich condition (Fig. 1(a), $\mu[O_2] = E[O_2]$ with $E[O_2]$ the total energy of an isolated oxygen molecule in its ground state) and the oxygen poor condition (Fig. 1(b), $\mu[O_2] = E[ZrO_2] - E[Zr]$). The formation energy for $ZrO_2:Fe$ is compared with the case of pure $ZrO_2$, $\Delta E_1(0, z)$ and $ZrO_2:Y$, $\Delta E_1(x_Y, z)$. To this end we considered different $V^\bullet\bullet_O$ concentrations and, for each, different $V^\bullet\bullet_O$ configurations. However we found that $\Delta E(x, z)$ is mainly determined by the kind of dopant, while the influence of the other parameters is lower. In Fig. 1 the changes due of these parameters results in different values for each system. While the $V^\bullet_O$ formation energy is negative in $ZrO_2:Y$ already in the oxygen rich case, in $ZrO_2:Fe$ films it is slightly positive, i.e. $\Delta E_{1}^{\text{tetra}} \approx 0.5 \text{ eV}$, but ten times lower than in pure $ZrO_2$. Varying the chemical potential from the oxygen rich to the oxygen poor configuration $\Delta E_{1}^{\text{tetra}}$ becomes negative, thus $Fe$ favors the formation of $V^\bullet\bullet_O$.

The creation of oxygen vacancies induces disorder in the system (see also the inset in Fig. [6]) thus the most symmetric phases are expected to be favored against the monoclinic phase. To evaluate this effect in Fig. 2 we consider the energy difference $\Delta E_2(x)$ between the tetragonal and the monoclinic phase as a function of the doping concentration, at fixed $y_{V^\bullet\bullet_O}/x = 0.5$. We look for the iron atomic percent, $x_{Fe}$, at which the tetragonal phase becomes favored.

The value of $\Delta E_2$ is very small and thus at the limit of the DFT–GGA resolution. The computed energy difference between the two phases at zero doping is $\Delta E_2(0) = 109 \text{ meV}/\text{f.u.}$, in agreement with previous works, (63 meV/f.u.\textsuperscript{20}, 144 meV/f.u.\textsuperscript{32}); the experimental estimation is 63 meV/f.u.\textsuperscript{33}. It is reasonable to assume that the trend of the energy difference is better computed than its absolute value and accordingly, assuming a constant “zero–doping
Figure 1. (color online) DFT (GGA) formation energy of oxygen vacancies (see Eq. 1) in ZrO$_2$:Y, ZrO$_2$:Fe and ZrO$_2$ in the two extrema case of (a) oxygen rich conditions and (b) oxygen poor conditions in both the tetragonal and the monoclinic structure. The doped systems are considered in the charge compensated configuration (i.e. $y_{V^\bullet\bullet/O} = 0.5$ for $X = Fe, Y$). The values are computed for different oxygen vacancies concentrations and also varying, for some concentrations, the position of the oxygen vacancies. In panels (a) and (b) histograms are presented in the same order (and colors).

The error" of $\approx 46 \text{ meV/f.u.}$ for every $Fe$ concentration, we can subtract it. Being $\Delta E_2$ of the order of few $\text{meV/f.u.}$ also the phonon energy of the two lattice could play a role. Indeed the monoclinic to tetragonal phase transition at $\approx 1440 \text{ K}$ can be explained in this terms$^{34,35}$. Thus we considered the energy difference of the lattice between the two structures for the undoped system. At room temperature however we found this contribution to be almost negligible, $\approx 5 \text{ meV/f.u.}$.

$\Delta E_2$ come out, instead, to be particularly sensitive to the chosen atomic configuration. Accordingly the data in Fig. 2 are scattered, with $\Delta E_2$ changing of few $\text{meV/f.u.}$ at given $x_{Fe}$. To extract the exact $x_{Fe}^{C}$ a statistical occupation of the different configurations should
Figure 2. (color online) DFT (GGA) total energy difference per formula unit between the tetragonal against the monoclinic phase for $\text{ZrO}_2:\text{Fe}$, panel (a), and $\text{ZrO}_2:\text{Y}$, panel (b). Total energies are computed for the charge compensated system (dots, $y_{V^\bullet\bullet}/X = 0.5$ for $X = \text{Fe}, \text{Y}$) changing the atomic configurations for each given concentrations. The shadowed areas are guides for the eyes while the continuous lines are a linear fit of the data. Also the results for the systems without oxygen vacancies (crosses, $y_{V^\bullet\bullet}/X = 0$) are shown for comparison. The zero level is shifted of (i) $-46 \text{ meV/f.u.}$ to align the energy difference at zero doping with the experimental value, (ii) $-5 \text{ meV/f.u.}$ to include the computed zero–point–energy difference of the two lattices.

be considered. However, to this end, one should sample a huge number of configurations, which is not feasible within DFT. In the present paper we assumed that, fixed $x_{Fe}$ and $z_{V^\bullet\bullet}$, changing the configurations for the $V_{O^\bullet\bullet}$, $\Delta E_2$ spans uniformly a given energy range ($E_R$) which can be extrapolated considering a limited number of configurations. $E_R$ is expected to increase, increasing the doping concentration, as an increasing number of configurations becomes available. With this assumptions $x_{Fe}^C$ was extracted considering the central value of the $E_R$.

In practice this was done with a linear fit of the data. In Fig. 2 to obtain the critical doping concentration, $\Delta E_2$ at zero doping is matched at the experimental value 63 $\text{ meV}$,
while the theoretical results would be 109 meV. The result, $x_{Fe}^C \approx 12\%$ at., can be compared with the case of $ZrO_2:Y$, where the same approach gives $x_{C}^C \approx 7\%$ at. which exactly matches the experimental value\textsuperscript{31}. We stress that with this approach the exact doping concentration can be affected by an error which can be as large as few atomic percent. What is significant here is the comparison of the two systems, i.e. $ZrO_2:Y$ and $ZrO_2:Fe$. Indeed both dopants, inducing oxygen vacancies favor the tetragonal against the monoclinic structure. However the two linear fits posses different slopes and we can conclude that iron is less efficient than yttrium in inducing a monoclinic to tetragonal phase transition. In Fig. 2 we also report the energy difference between the monoclinic and the tetragonal phase for the case without oxygen vacancies, i.e. $y_{V_{O}^{\bullet\bullet}/X} = 0$. In this configuration we found that the local structure of the crystal is much less distorted by doping and accordingly the variation of the energy difference between the two phases is small. This confirms that a key role in the monoclinic to tetragonal phase transition is played by oxygen vacancies\textsuperscript{31} and not by the dopant itself.

### B. Electronic properties

Given the results of the previous section and the fact that experimentally we describe a system at high doping concentration, which we found to be in the tetragonal phase, in the description of the electronic properties of the system we focus our attention on the tetragonal structure of $ZrO_2:Fe$.

The main difference between $Y$ and $Fe$ is the presence of the unfilled $Fe(d)$ orbitals which, falling inside the energy gap of zirconia, determine the electronic properties of the doped system. The $d$–orbitals occupation is also strongly affected by $V_{O}^{\bullet\bullet}$ and is used here, together with the computed magnetic moment, to infer the $Fe$ oxidation state. At $y_{V_{O}^{\bullet\bullet}/Fe} = 0$, $Fe$ acts as an acceptor (Fig. 3(a)) with the creation of holes in the majority spin VB. These are preferentially located on the $Fe(d)$ orbitals as shown by the projected–DOS with the projection of the hole states on the $d$–orbitals close to 0.5. Thus $Fe$ is forced in the $Fe^{+4}$ oxidation state with a magnetic moment per atom equal to 4 Bohr magnetons ($\mu_B$). The creation of $V_{O}^{\bullet\bullet}$ release the electrons captured by the $O$ anions. At $y_{V_{O}^{\bullet\bullet}/Fe} = 0.5$ the system turns into a charge–transfer semi–conductor (see Fig. 3(b)), i.e. the $V_{O}^{\bullet\bullet}$ do not create an impurity bands, as it would happen in $ZrO_2$, but compensate the holes in the $Fe(d)$ orbitals. In this configuration $Fe$ atoms are in the $+3$ oxidation state and the magnetic moment per
Figure 3. (color online) Total (full line) and $d$–orbital projected (dashed line) density of states (DOS) at the GGA level of ZrO$_2$:Fe at $x_{Fe} = 25\%$ with $y_{V^{••}/Fe}$ equal to respectively 0 (panel a), 0.5 (panel b), 1 (panel c). The vertical dashed line marks the Fermi level. The Fermi level of panel (b) is the zero of the energy axis, while in panels (a) and (c) the zero is obtained aligning the bottom of the valence band at $\approx -6.5$ eV as in panel (b).

iron atom is maximized, 5 $\mu_B$. If $y_{V^{••}/Fe}$ exceeds 0.5, electrons start to fill the minority $Fe(d)$ levels. This decreases the average magnetic moment, while the system reverts to an half–metal. At $y_{V^{••}/Fe} = 1$ (Fig. 3(c)) all iron atoms are in a +2 oxidation state with the per atom magnetic moment equal to 4 $\mu_B$. In Fig. 3 we also notice that at $y_{V^{••}/Fe} \leq 0.5$ no extra state, other than the $Fe(d)$ orbitals, appears between the valence and the conduction band of ZrO$_2$. Only when $y_{V^{••}/Fe} > 0.5$ (Fig. 3(c)) such a state exists. The latter can be
associated to an impurity band which has been suggested to create bound magnetic polarons in case of magnetic doping. However the configuration $y_{V\cdot\cdot\cdot O}/Fe = 1$ is not favored. Indeed the energy cost, for each extra $V\cdot\cdot\cdot O$ created in the system, of the reaction

$$Zr_{1-x}O_{2-x/2}Fe_x \rightarrow Zr_{1-x}O_{2-x}Fe_x + \frac{x}{4}\mu[O_2]$$

changes from $\approx 2.5$ eV, oxygen rich conditions, to $\approx 0$ eV, oxygen poor conditions, thus remaining positive for any value of the oxygen chemical potential. As for the $V\cdot\cdot\cdot O$ formation energy $\Delta E_1$, this value is weakly dependent on the atomic doping $x_{Fe}$. Last but not least, even if in this case the impurity band exist, it is empty. Thus the possible existence of bound magnetic polaron in $ZrO_2:Fe$ is unlike. We will also show in the next section that, experimentally, iron in $ZrO_2:Fe$ is in the $Fe^{+3}$ and not in the $Fe^{+2}$ oxidation state.

We remark that, even if at $y_{V\cdot\cdot\cdot O}/Fe = 0$ and $y_{V\cdot\cdot\cdot O}/Fe = 1$ the system is metallic, the per atom magnetic moment is integer. The reason is that in both cases $ZrO_2:Fe$ is indeed an half–metal and thus electrons can move across the Fermi level only in one spin channel. We have verified this result increasing the sampling of the k–points grid from $2x2x2$ to $3x3x3$ in the 96 super–cell and from $4x4x4$ to $8x8x8$ in the 12 atoms super–cell. In both cases the system remains metallic, with fractional occupation in the majority ($y_{V\cdot\cdot\cdot O}/Fe = 0$) or minority ($y_{V\cdot\cdot\cdot O}/Fe = 1$) spin channel (a smearing of 0.002 Ry was used in the self–consistence cycle in this case), but with constant per atom magnetic moment $m_z = 4\ \mu_B$. In principle the 96 atoms super–cell with a sampling $3x3x3$ is equivalent to the 12 atoms supercell with sampling $6x6x6$. However the two could differ because in the 96 atoms super–cell, removing symmetries, disorder is taken into account. This could for example induce a localization of holes on the Fe atoms. Thus the convergence check were also a rough way to explore possible Anderson–like localization mechanisms. However we did not observe such phenomena.

These are the prediction of the GGA. However for TM oxides this approximation is known to suffer of some deficiencies. In particular it suffers of the well known problem of self–interaction, which tends to delocalize too much the $d$ orbitals. A common way to avoid this problem is to correct the DFT scheme with a Hubbard like term $U$ which enters as an external parameter. The value of $U$ is system dependent and should be optimized either with a direct comparison with experimental data or with a self–consistent approach. In the literature usually $U = 1 – 3$ eV for elemental iron and $U = 2 – 6$ eV in iron oxides. For example Cococcini et al. report, after a self–consistent calculation, $U \approx 2.2$ eV for metal
iron and $U = 4.3\ eV$ for FeO. Here we begin choosing an intermediate value, $U = 3.3\ eV$, in order to evaluate the physical effects introduced by this correction.

In Fig. 4 we plot the DOS for the GGA+$U$ approach at $y_{V_{\text{O}}}/F_{\text{e}} = 0, 0.5, 1$. We can directly compare the results with the GGA DOS plots in Fig. 3. As expected the $U$ correction pushed down the occupied $d$ level and a sharp structure appeared in the DOS just below the VB of $ZrO_2$:Fe. Also the crystal field splitting of the spin minority $d$ orbitals, between
the $e_g$ and the $t_g$ states, was reduced, and is not distinguishable anymore with the smearing parameter used in the plot; with the exception of the case $y_{V_o^{••}/Fe} = 1$. However in the charge–compensated situation, $y_{V_o^{••}/Fe} = 0.5$, these corrections do not alter the qualitative description of the system, which remains a magnetic semi-conductor with the magnetic moment per atom maximized. Instead, when we deviate from this configuration, we notice two important differences. For $y_{V_o^{••}/Fe} < 0.5$ the holes created in the VB are less localized on the Fe atoms. Indeed the projection of the hole states on the $d$–levels drops from $\approx 0.5$ (GGA) to less than 0.1 (GGA+$U$). Thus iron is in the $Fe^{3+}$ configuration, while the holes are in the $ZrO_2$ VB, i.e. on the oxygen atoms. Accordingly the $V_o^{••}$ formation energy drops from 0.5 eV (GGA) to 0.0 eV because oxygen atoms are more weakly bound to the system. For $y_{V_o^{••}/Fe} > 0.5$ the extra electrons start to fill the minority $d$-levels, as in the GGA case. However the newly occupied levels are pushed down in energy and thus the system is not metallic but it displays an energy gap, i.e. GGA+$U$ predicts a a Mott insulator in this case. Also for the $GGA+U$ case we verified that in the metallic case (i.e. at $y_{V_o^{••}/Fe} = 0$) the value of the magnetic moment remains constant improving the sampling of the Brillouin zone.

The electronic properties in the present section were reported for $x_{Fe} = 25\%$. We did not find significant changes for the other doping concentrations, at least for $y_{V_o^{••}/Fe} = 0.5$. At the lowest computed doping concentration however, $x_{Fe} = 6.25\%$, the Fe atoms are too far apart and the localized $d$–levels do not create a band. Thus the metallic phases predicted within GGA ($y_{V_o^{••}/Fe} = 0, 1$) become semi-conducting phases with defects states localized close to the Fermi level.

III. EXPERIMENTAL RESULTS

A. Structural characterization

Experimentally, as a first step, we first studied the structural properties of the films growth by atomic layer deposition. In Fig. 5 the ToF–SIMS depth profile of a representative film (namely, $ZrO_2:Fe$ at $x_{Fe} = 20\%$ at.), including Fe, $FeO$, $ZrO$ and $Si$ negative secondary ion intensity profile is graphed. Fe and $FeO$ are both used as representative of Fe distribution along the film thickness; in particular $FeO$ ion fragment has not to be
considered as a mark of FeO chemical compound in the film, but as a fingerprint of Fe embedded in the ZrO$_2$ host matrix. The flatness of ZrO and Fe related profiles indicates that the film grows uniformly during the ALD process, without changes in the distribution of the chemical species, evidencing that the growth process is well controlled. Further, Si diffusion in ZrO$_2$ is excluded with a well distinct film/substrate interface, an indication that the substrate does not affect ZrO$_2$:Fe properties both during the film growth and the thermal treatment. Furthermore, the Fe profile is almost constant, thus it is the doping in the film, and the absence of large fluctuations such as peaked maxima, can exclude Fe clustering. Indeed the latter would have been observed as a sudden increase of Fe intensity with a concomitant abrupt decrease of FeO intensity, indicating that an Fe rich / O poor environment is detected. Instead both Fe and FeO signals mimic the same profile shape, confirming that Fe is uniformly diluted within the ZrO$_2$ matrix.
Figure 6. (color online) - XRD patterns of $\text{ZrO}_2$ (blue) and $\text{ZrO}_2:Fe$ (red) ($\text{Fe}$ doping $\approx 20\%$ at.) films evidencing Fe doping is effective in suppressing the monoclinic phase. $t(\text{ZrO}_2)$ and $m(\text{ZrO}_2)$ indicates the reflections from reference tetragonal and monoclinic $\text{ZrO}_2$, respectively. On the right the relaxed DFT structure for $m(\text{ZrO}_2)$, $t(\text{ZrO}_2)$ and $t(\text{ZrO}_2:Fe)$ at $x_{Fe} = 25\%$ at. represented with the xcrysden package (see Ref. 39); Zr atoms in blue, Fe atoms in red and the smaller O atoms in black.

To get details on the film crystalline structure, in Fig. 6 we compare the XRD patterns of $\text{ZrO}_2$ and $\text{ZrO}_2:Fe$. Both films mainly present the cubic/tetragonal phase. Indeed in these films there is a balance between the bulk energy, where the monoclinic phase is favored, and the surface energy, where the tetragonal phase is favored. The critical grain size\textsuperscript{36,37} below which the tetragonal phase become the most favored is $\approx 15 \text{ nm}$. In our films, being the grain size close to the film thickness (from XRD data), we are close to this critical value. This can be evinced from the XRD patterns of pure $\text{ZrO}_2$ where the peaks of the monoclinic phase are also evident. However in the $\text{ZrO}_2:Fe$ films the monoclinic phase is completely suppressed, confirming our theoretical findings. Even from these measures there
Figure 7. (color online) (a): The Fe\(^{2p}\) core level photo-emission spectra in ZrO\(_2\):Fe. (b): Fe\(^{3p}\) and Zr\(^{4s}\) photo-emission spectra and computed DOS for ZrO\(_2\):Fe with \(y_{\text{O}/\text{Fe}}\) equal to 0 (green dashed), 0.5 (red continuous), 1 (black dot-dashed). The Fe\(^{3p}\) majority spin level is in light gray. (c): Measured and computed valence band (VB) for pure ZrO\(_2\). (d): Measured VB for ZrO\(_2\):Fe. Computed VB for ZrO\(_2\):Fe with Fe doping substitutional at \(y_{\text{O}/\text{Fe}} = 0.5\) (continuous red line) or interstitials (dashed maroon line). In panels (b)-(c)-(d) the experimental data (and fit) are vertically shifted respect to the DFT-DOS. All DOS are obtained at within the GGA. The experimental data were collected with the PHI 5600 instrument (see details in sec. I B).

is no indication of segregated iron phase or iron oxide clusters.

**B. Electronic properties**

In Fig. 7 we report the high resolution spectra of the Fe\(^{2p}\) core level (a), the Fe\(^{3p}\) semi-core (b) levels and the VB (c-d). In Fig. 7(a-b) the data were fitted with a doublet of asymmetric Voigt functions for the two main peaks plus a Voigt function for the satellite on top of a Shirley background and in Fig. 7(b-d) the spectra are compared with DFT(GGA)-
Table I. Energy distances [eV] from $Fe(2p_{3/2})$.

Data for iron oxides from Ref. 43

|            | $Fe_2O_3$ | $Fe_3O_4$ | $FeO$  | $ZrO_2:Fe$ |
|------------|-----------|-----------|--------|------------|
| $Fe(2p_{1/2})$ | -13.6     | -13.5     | -13.6  | -13.5      |
| satellite  | -7.8      | not pres. | -6.0   | -8.6       |
| $Fe(3p)$   | 655.4     | not av.   | 653.9  | 655.2      |

DOS computed as described in sec. I A.

The change of the XPS–VB from $ZrO_2$ (blue) to $ZrO_2:Fe$ (red) is in agreement with the DFT(GGA)–DOS obtained considering substitutional iron doping. In particular experimentally the double peak structure of pure $ZrO_2$ is suppressed with doping. Theoretically this behavior is reproduced only assuming substitutional doping.

The core or semi–core levels of TM usually show a structured shape due to, at least, four factors: the spin–orbit (SO) splitting, the exchange splitting, the multiplet splitting and the $eh$ screening to the core–hole. The SO term is responsible for the $2p_{1/2}$ - $2p_{3/2}$ splitting $\Delta E_{SO} = 13.5$ eV and is not sensitive to the chemical environment (see Fig. 7(a)). The exchange and multiplet splitting instead give the characteristic asymmetric shape of the XPS peaks in metals. Finally the screening effect, which is strongly sensitive to the chemical environment$^{40–42}$, can create satellites. For the $Fe(2p)$ core level the distance between the satellite and the $Fe(2p_{3/2})$ peak is a marker of the iron oxidation state$^{43}$. Also the position of the $Fe(3p)$ peak (Fig. 7(b)) is sensitive to the $Fe$ chemical environment$^{43}$. The comparison with the values of Ref. 43, reported in Table I shows that iron is in the $Fe^{+3}$ oxidation state.

According to our DFT results the $Fe$ oxidation state is strongly related to the presence of $V_O^{**}$ in the system (see Fig. 3). To better describe this point we study the $Fe(3p)$ semi–core levels with first principles simulations. Indeed the $Fe(3p)$ wave–functions are spatially localized close to the $Fe(3d)$, which are in valence, and so are very sensitive to the chemical environment. The energy of the $Zr(4s)$ level is used as a reference to properly align the experimental XPS levels with the theoretical DOS.

In our approach the SO coupling term was included, both in the pseudo–potentials and in the hamiltonian, while the multiplet and the exchange splitting were accounted for by the exchange–correlation (xc) potential. For the $Fe(3p)$ level we found $\Delta E_{SO} \leq 1$ eV, while
$\Delta E_{xc} \approx 5 \text{ eV}$ between the spin minority and the spin majority which is clearly visible in Fig. 7(b). This is overestimated by DFT. In the case of semi–core levels Takahashi et al. showed that the screening effects, which are not included in the present approach, gives a broadening and a shift of the majority spin channel with, possibly, the creation of satellites. Indeed we can suppose that these effects would correct the overestimated $\Delta E_{xc} \approx 5 \text{ eV}$, shifting the majority–spin energy level close to the minority one giving a single asymmetric peak with higher intensity as in the experimental case. However such an approach is beyond the scope of the present work. The minority–spin channel instead is less affected by screening effects retaining the independent–particle structure with the onset of the spectrum due to absorption from this channel. Thus we compared the energy position of the minority DOS with the measured Fe(3p) XPS spectrum. In our simulations the distance of the Fe(3p) minority peak from the Zr(4s) level, $\Delta E_y$, is strongly dependent on $y_{O/Fe}$ with $\Delta E_{y=0} = 1.8$, $\Delta E_{y=0.5} = 3.1$ and $\Delta E_{y=1} = 4.0 \text{ eV}$. The value $\Delta E_{y=0.5}$, i.e. the configuration with iron in the Fe$^{+3}$ oxidation state, best agrees with the experimentally measured splitting $\Delta E = 2.9 \text{ eV}$, in agreement with the conclusion drawn from Table II and in general from sec. II.

In sec. III we showed that the electronic properties and in particular the shape of the valence band could be strongly influenced by the on–site electronic correlation, by the comparison of GGA and GGA+$U$ predictions at $U = 3.3 \text{ eV}$.

To decide which of the two scenarios, GGA or GGA+$U$, better describes the experimental situation we compared the obtained DOS for the charge–compensated case with the measured photo–emission from the VB; the values $U = 0.0, 1.0, 2.0, 3.3 \text{ eV}$ are here considered. To mimic the experimental spectrum, we have superimposed to the DFT–DOS a Shirley like background, i.e. a background proportional to the integral of the DOS. Also, for a quantitative comparison, we computed the theoretical DOS for $y_{O/Fe} = 0.5$ and $x_{Fe} = 18.75\%$, which is the theoretical value closest to the experimental measured doping.

In Fig. 8 we see that the structure which identifies the $d$ levels in the GGA+$U$, at the reference value $U = 3.3 \text{ eV}$, is not present experimentally and the agreement between theory and experiment is much better in the standard GGA (i.e. $U = 0. \text{ eV}$). At the intermediate values $U = 1.0 \text{ eV}$ and $U = 2.0 \text{ eV}$ such structure is not visible, however the agreement with the experimental results is worse than for the $U = 0. \text{ eV}$ case. We can conclude that the value $U = 0$ best agrees with the photo–emission VB, and that, given the experimental
Figure 8. (color online) Valence band of $\text{ZrO}_2:Fe$. The GGA+$U$ scheme at $x_{Fe} = 18.75\%$, $y_{V_{O}^{**}/Fe} = 0.5$, for the values of $U = 0.0, 1.0, 2.0, 3.3$, is compared against experimental data. The smearing parameter used for the plot is 0.06 Ry. The experimental data were collected with the PHI 5600 instrument (see details in sec. IB).

resolution, the optimal choice of $U$ must be between 0 and 1 eV. Thus in $\text{ZrO}_2:Fe$ the effect of the self–interaction of the $d$ orbitals, which is corrected by the Hubbard $U$ term, is smaller than in common iron oxides. This is an “a posteriori” justification of the results obtained, in the present work, within the GGA.

IV. CONCLUSIONS

In conclusion we studied iron doped zirconia both theoretically, with first–principles simulations, and experimentally, with structural, chemical and electronic characterization of thin films grown by atomic layer deposition.

As expected from simple considerations, iron was found experimentally in the $Fe^{+3}$ oxidation state. We also found that it induces a monoclinic to tetragonal phase transition. Theoretically the oxidation state was related to presence of oxygen vacancies which play a
key role in the structural phase transition. The theoretical findings have been tested with a detailed comparison against photo-emission spectra of the samples grown by atomic layer deposition to validate the assumptions. These results are a confirmation that iron doped zirconia could be a good candidate in view of oxygen sensing applications as reported in the past.

Moreover the presence of vacancies is seen not only to influence the structure of the system but, theoretically, also to determine the density of states at the Fermi level and the eventual presence of impurity states in the gap which could be associated to magnetic polarons. In particular, we discussed how the ratio between oxygen vacancies and the iron atoms concentration shifts the Fermi level of the system. We found that in the most stable configuration, the $Fe^{+3}$ iron atoms are charge-compensated by the presence of oxygen vacancies with a ration of 0.5, i.e. one vacancy each two iron atoms. The resulting system is a semi-conductor with no impurity state in the gap.

These results should be considered for a correct description of the behavior of iron doped zirconia, or more in general of high-k oxides doped with valence +3 elements, in resistive switching devices. Moreover the absence of impurity states rules out the magnetic polaron model as a possible mechanism to explain the magnetic properties of the system.

Finally we have explored the importance of the Hubbard U correction. Indeed, theoretically, varying the value of U from 0 eV to 3.3 eV the electronic properties of the system change significantly. We showed that in iron doped zirconia the value $U \approx 0$ eV best agrees with the experimental data, thus indicating that the on site electronic correlation is low in this system.

AKNOWLEDGMENTS

This work was funded by the Cariplo Fundation through the OSEA project 2009-2552. D.S. and A.D. would like to acknowledge G. Onida and the ETSF Milan node for the opportunity of running simulations on the “etsfmi cluster”, P. Salvestrini for technical support on the cluster and A. Molle and S. Spiga for useful comments and discussions. We also
acknowledge computational resources provided under the project MOSE by CASPUR.

1 H. Ohno, H. Munekata, T. Penney, S. Von Molnar, and L. L. Chang, Phys. Rev. Lett. 68, 2664 (1992)
2 H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto and Y. Iye, Appl. Phys. Lett. 69, 363 (1996)
3 J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nature Materials 4, 173 (2005)
4 K. Sato, L. Bergqvist, J. Kudrnovsky, P. H. Dederichs, O. Eriksson, I. Turek, B. Sanyal, G. Bouzerar, H. Katayama-Yoshida, V. A. Dinh, T. Fukushima, H. Kizaki, R. Zeller, Rev. Mod. Phys., 82, 1633 (2010)
5 H. P. Gunnlaugsson, T. E. Mlholt, R. Mantovan, H. Masenda, D. Naidoo, W. B. Dlamini, R. Sielemann, K. Baruth-Ram, G. Weyer, K. Johnston, G. Langouche, S. Olafsson, H. P. Gislason, Y. Kobayashi, Y. Yoshida, M. Fanciulli, and ISOLDE Collaboration, Appl. Phys. Lett. 97, 142501 (2010)
6 N. H. Hong, N. Poirotet, and J. Sakai, Appl. Phys. Lett. 89, 042503 (2006)
7 N. H. Hong, C.-K. Park, A. T. Raghavender, O. Ciftja, N. S. Bingham, M. H. Phan, and H. Srikanth, J. Appl. Phys. 111, 07C302 (2012)
8 N. H. Hong, J. Sakai, N. Poirot, and A. Ruyter, Appl. Phys. Lett. 86, 242505 (2005)
9 J. M. D. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, L. S. Dorneles, Phys. Rev. B 72, 024450 (2005)
10 V. V. Kriventsov, D. I. Kochubey, Y. V. Maximov, I. P. Suzdalev, M. V. Tsodikov, J. A. Navio, M. C. Hidalgo, G. Colón, Nuclear Instruments and Methods in Physics Research A 470, 341 (2001)
11 T. R. Sahoo, S. S. Manoharan, S. Kurian, and N. S. Gajhiye, Hyperfine Interaction 188, 43 (2009)
12 S. Ostanin, A. Ernst, L. M. Sandratskii, P. Bruno, M. Dâne, I. D. Hughes, J. B. Staunton, W. Hergert, I. Mertig, and J. Kudrnovský, Phys. Rev. Lett. 98, 016101 (2007)
13 T. Archer, C. D. Pemmaraju, and S. Sanvito, Journal of Magnetism and Magnetic Materials 316, e188-e190 (2007)
14 N. H. Hong, J. Sakai, N. T. Huong, N. Poirot, and A. Ruyter, Phys. Rev. B 72 045336 (2005)
15 G. Stefanic, B. Grzeta, S. Music, Mat. Chem. and Phys. 65, 216 (2000)
16 W. Cao, O. K. Tan, W. Zhu, B. Jiang, C. V. Gopal Reddy, Sensors and Actuators B 77, 421 (2001)
17 W. Cao, O. K. Tan, J. S. Pan, W. Zhu, C. V. Gopal Reddy, Mat. Chem. and Phys. 75, 67 (2002)
18 H. Zhang, B. Gao, B. Sun, G. Chen, L. Zeng, L. Liu, X. Liu, J. Lu, R. Han, J. Kang, and B. Yu Appl. Phys. Lett. 96, 123502 (2010)
19 S. Spiga, R. Rao, L. Lamagna, C. Wiemer, G. Congedo, A. Lamperti, A. Molle, M. Fanciulli, F. Palma, and F. Irrera J. Appl. Phys. 112, 014107 (2012)
20 G. Stapper, M. Bernasconi, N. Nicoloso, and M. Parrinello, Phys. Rev. B 59, 797 (1999)
21 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scandolo, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, J. Phys.:Condens. Matter 21, 395502 (2009)
22 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
23 P. Hohenberg, and W. Kohn, Phys. Rev. 136, B864 (1964)
24 W. Kohn, and L. J. Sham, Phys. Rev. 140, A1133 (1965)
25 D. Vanderbilt, Phys. Rev. B 41, 7892R (1990)
26 A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B 41, 1227R (1990)
27 C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B 58, 3641 (1998)
28 X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côtè, T. Deutsch, L. Genovese, Ph. Ghosez, M. Giantomassi, S. Goedecker, D.R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazeve, M.J.T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M.J. Verstraete, G. Zerah, J.W. Zwanziger, Comp. Phys. Comm. 180, 2582 (2009)
29 A. Lamperti, E. Cianci, R. Ciprian, D. Sangalli, and A. Debernardi, Thin solid films (2012), in press http://dx.doi.org/10.1016/j.tsf.2012.11.127
30 A. Lamperti, L. Lamagna, G. Congedo, and S. Spiga, J. Electrochem. Soc., 158, G211 (2011)
31 D. Sangalli, and A. Debernardi, Phys. Rev. B 84, 214113 (2011)
32 J. K. Dewhurst, and J. E. Lowther, Phys. Rev. B 57, 741 (1998)
33 R. J. Ackermann, E. G. Rauth, and C. A. Alexander, High. Temp. Sci. 7, 304 (1975)
34 A. Debernardi, C. Wiemer, M. Fanciulli, Materials Science in Semiconductor Processing 11, 241-244 (2008)
35 X. Lou, W. Zhou, S. V. Ushakov, A. Navrotsky, and A. A. Demkov, Phys. Rev. B 80, 134119 (2009)
36 A. Christensen, and E. A. Carter, Phys. Rev. B 58, 8050 (1998)
37 G. Cerrato, S. Bordiga, S. Barbera, and C. Morterra, Surf. Sci. 50, 377 (1997); Appl. Surf. Sci. 53, 115 (1997).
38 International Crystal Structure Database, FIZ Karlsruhe and NIST ed., Release 2010 Code #68589 (t-ZrO$_2$) and #89426 (m-ZrO$_2$)
39 A. Kokalj, Comp. Mater. Sci. 28, 155 (2003)
40 D.-J. Huang, D. M. Riffe, J. L. Erskine, Phys. Rev. B 51, 15170 (1995)
41 M. Takahashi, and J.-I. Igarashi, Phys. Rev. B 81, 035118 (2010)
42 A. K. See, and L. E. Klebanoff, Phys. Rev. B 51, 7901 (1995)
43 T. Yamashita, and P. Hayes, Appl. Surf. Science 254, 2441 (2008)
44 M. Cococcioni, and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005)