Structural, electronic, and hyperfine properties of pure and Ta-doped m-ZrO$_2$

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(Received 8 November 2011; revised manuscript received 20 January 2012; published 6 April 2012)

A combination of experiments and $ab$ initio quantum-mechanical calculations has been applied to examine electronic, structural, and hyperfine interactions in pure and Ta-doped zirconium dioxide in its monoclinic phase ($m$-ZrO$_2$). From the theoretical point of view, the full-potential linear augmented plane wave plus local orbital (APW + lo) method was applied to treat the electronic structure of the doped system including the atomic relaxations introduced by the impurities in the host in a fully self-consistent way using a supercell approach. Different charge states of the Ta impurity were considered in the study and its effects on the electronic, structural, and hyperfine properties are discussed. Our results suggest that two different charge states coexist in Ta-doped $m$-ZrO$_2$. Further, $ab$ initio calculations predict that depending on the impurity charge state, a sizeable magnetic moment can be induced at the Ta-probe site. This prediction is confirmed by a new analysis of experimental data.

DOI: 10.1103/PhysRevB.85.155202 PACS number(s): 71.15.Mb, 76.80.+y, 71.20.Nr

I. INTRODUCTION

Zirconium dioxide (zirconia) is one of the most important compounds in materials science and technology because it combines excellent mechanical, thermal, chemical, and dielectric properties: high melting point ($2700\,^\circ$C), low thermal and electronic conductivity, good oxygen-ion conductivity at elevated temperatures, high strength and enhanced fracture toughness, chemical inertness, and resistance to corrosion, high dielectric constant, etc. Additionally, ZrO$_2$ shows a rich variety of crystal structures depending on pressure, temperature, impurity or doping content, growth conditions, etc. In its various forms and (sometimes) with the addition of small amounts of impurities, ZrO$_2$ has applications, for example, in refractory materials, solid oxide fuel cell electrolytes, catalyst substrates, protective coatings, functional ceramics, ceramic glazes, oxygen sensors, electro-ceramics, and abrasives and grinding media, etc. Additionally, ZrO$_2$ has been extensively studied by different experimental and theoretical techniques in recent years (see, for example, Ref. 15 and references therein).

Magnetic effects in oxides have gained considerable attention in recent years due to their promising applications in spintronic devices. In addition to its potential utility, the study of spin-polarized transport is revealing new fundamental physics. In particular, Coey et al. reported ferromagnetism above room temperature in undoped HfO$_2$ thin films fabricated by conventional out-of-equilibrium pulsed-laser deposition. Such unexpected ferromagnetism has also been reported in CaO, ZnO, CaB$_6$, and ZrO$_2$ thin films and nanoparticles. From a theoretical point of view, it has been shown that point defects such as cation or oxygen vacancies or electron trapping at an impurity site can be the origin of the magnetism. Very recently, a combination of hyperfine experiments [using time-differential perturbed angular correlations spectroscopy (TDPAC) with $^{181}$Ta as a probe] and $ab$ initio calculations has been applied to study the electronic structure of Ta-doped hafnium dioxide. The study revealed that Ta introduces impurity levels in the band gap of semiconducting monoclinic HfO$_2$ ($m$-HfO$_2$), and induces significant structural distortions in the host lattice. Also, the structural relaxations as well as the hyperfine parameters strongly depend on the charge state of the impurity. Moreover, the combination of experiments and theory suggests that two different charge states coexist in this compound, and depending on the impurity charge state a sizeable magnetic moment can be induced at the probe site. These results indicate that the trapping of an electron at a cationic site can induce a magnetic moment localized at this site. This trapping effect could be related to the magnetism observed in thin films of pure $m$-HfO$_2$. ZrO$_2$ and HfO$_2$ are similar systems regarding their chemical and physical properties. They have the same crystallographic structures with very similar cell parameters and atomic dopants, and both can be stabilized in their more symmetric structures by means of the addition of low percentages of dopants. Both compounds were studied with TDPAC using $^{181}$Ta as a probe (see, for example, Refs. 33,34, and references therein). In consequence, the extension of the combined experimental and theoretical studies to $m$-ZrO$_2$ is of great interest.

In this work, we present an $ab$ initio study in pure and Ta-doped $m$-ZrO$_2$ including spin-polarized calculations for different charge states. Force calculations were applied to optimize the doped structures relaxing all the atomic positions in the supercell (SC) approximation. From the self-consistent potentials, hyperfine parameters at the Ta site were derived. The influence of the impurity charge state on the hyperfine
parameters and the magnetic state is analyzed. Our results are compared to different experimental and theoretical results reported in the literature and a new analysis of a previous TDPAC experiment is performed.

II. THE SYSTEM UNDER STUDY

Zirconium dioxide is the only thermodynamically stable compound in the system Zr-O.\textsuperscript{35,36} At low pressures, zirconia displays three phases: monoclinic, tetragonal, and cubic. The ground-state phase of zirconia, a baddeleyite structure with a monoclinic unit cell, is stable up to around 1480 K. The

![Diagram of monoclinic lattice structure of $m-ZrO_2$.](image)

The unit cell has dimensions $a = 5.1505\,\text{Å}$, $b = 5.2116\,\text{Å}$, $c = 5.3173\,\text{Å}$, and $\beta = 99.230^\circ$. In this arrangement the Zr atoms exhibit a sevenfold coordination with Zr-O bond lengths between 2.03 and 2.26 Å. There are two kinds of oxygen atoms, which have different coordination: oxygen type 1 (O1) having three Zr neighbors between 2.03 and 2.17 Å, and type 2 (O2) having four Zr neighbors between 2.16 and 2.26 Å (See Fig. 1). The shortest O-O distance is 2.57 Å.

III. HYPERFINE PARAMETERS

Nuclear techniques, such as TDPAC or nuclear magnetic resonance (NMR), among others, have been extensively applied to the study of materials in order to elucidate the (sub-)nanoscopic scale environment(s) of impurities or constituent atoms of solids (see Ref. 38 and references therein). What is most rewarding in these methods is their “ability” to measure charge symmetry-related properties, such as the electric field gradients (EFG), as well as magnetic properties, such as magnetic hyperfine fields ($B_{HF}$), making it possible to obtain a fingerprint of the electronic and magnetic configuration near and at the probe nucleus.\textsuperscript{39}

![Diagram of O atoms in the ZrO$_2$ polyhedra in m-ZrO$_2$.](image)
The information provided by these techniques is given as a product of a nuclear and an external nuclear quantity.\(^{39}\) In the case of pure electric quadrupole interactions, the nuclear quantity is the nuclear quadrupole moment \(Q\), characteristic of a given nuclear state of spin \(I\), which interacts with the EFG at the nuclear position. The EFG tensor is a rank 2 traceless symmetric tensor whose components, denoted by \(V_{ij}\), are defined by the second derivative (with respect to the spatial coordinates) of the Coulomb potential \(V(r)\) created by the charge density surrounding a given nucleus.\(^{39}\) In the principal axis system the three diagonal components of the EFG tensor are labeled according to the conventional choice \(|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|\). Hence, \(V_{ZZ}\) is the largest eigenvalue of the EFG tensor. The measured magnitude is the nuclear coupling constant frequency \(\nu_Q\), related to \(V_{ZZ}\) by\(^{39}\)

\[
\nu_Q = \frac{eQ}{\hbar}V_{ZZ},
\]

The EFG tensor is completely specified by \(V_{ZZ}\), together with the asymmetry parameter \(\eta\):

\[
\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}},
\]

where \(Q = 2.36(5)\) b for the spin \(5/2\) 482 keV excited state of \(^{181}\)Ta (TDPAC-sensitive state, Ref. 40), while \(Q = -0.176(3)\) b is the nuclear quadrupole moment of the spin \(5/2\) ground state of \(^{91}\)Zr (sensitive state in NMR spectroscopy, Ref. 41).

The magnetic hyperfine interaction is caused by the coupling between the magnetic field produced by the electron spin and the orbital currents at the probe site and the magnetic moment of the nucleus. The experimentally observed quantity is, in this case, the precession frequency:\(^{39}\)

\[
\omega_L = \frac{g_N\mu_N B_{HF}}{\hbar},
\]

where \(g_N\) denotes the nuclear \(g\) factor and \(\mu_N\) is the nuclear magneton.\(^{42}\) \(B_{HF}\) is the magnetic hyperfine field, which is a fingerprint of the magnetic configuration and the spin polarization near and at the probe nucleus.\(^{39}\)

Whereas pure quadrupolar and/or pure magnetic interactions have been extensively observed using TDPAC, cases of combined electric and magnetic interaction (CEMI) in which the quadrupolar electric and the dipolar magnetic interactions are of the same order of magnitude are scarce in the literature.\(^{43,44}\) In the case of a CEMI, the experimentally observed parameters are \(\nu_Q\), the asymmetry parameter \(\eta\), the magnetic frequency \(\omega_L\), and the Euler angles \(\beta, \gamma\), which describe the relative orientation of the magnetic hyperfine field and the EFG tensor.

IV. CALCULATION DETAILS

We performed \textit{ab initio} electronic structure calculations to determine the self-consistent potential and the charge density inside the \(m\)-ZrO\(_2\) cell. From these \textit{ab initio} calculations the hyperfine parameters at a Ta impurity replacing Zr were obtained, taking properly into account the structural and electronic effects introduced by the impurity in the host lattice.

We simulated this nonperiodic system by considering a periodically repeated large unit cell where a single Ta atom replaces a single Zr in the monoclinic ZrO\(_2\) host (the SC method). From these \textit{ab initio} calculations we obtained the equilibrium relaxed structures and the EFG tensor corresponding to a Ta atom at the cation site in the ZrO\(_2\) lattice. The calculations were made for a periodic arrangement of 96-atom SCs, each constructed from eight unit cells of \(m\)-ZrO\(_2\). The resulting 96-atom SC has dimensions \(d' = 2a = 10.3010\) Å, \(b' = 2b = 10.4062\) Å, and \(c' = 2c = 10.6308\) Å. The replacing of a single Zr atom in the SC by one Ta atom lead to an ordered compound, \(\text{Zr}_0.96\text{Ta}_{0.03}\text{O}_2\), representing about 3 at. % doping. Similar to the case of Ta in \(m\)-HfO\(_2\), additional calculations were performed (for some selected cases) using larger SCs. These additional calculations show that although a 3 at. % doping is large compared to parts per million (ppm) dilutions in the samples used in the TDPAC experiments, the choice of the 96-atom SC keeps the Ta atoms sufficiently far from each other (10.3 Å) to avoid significant interactions. Thus, the 96-atom SC is an excellent compromise between computational times and accuracy of the calculations.

To solve the scalar-relativistic Kohn-Sham equations, calculations based on the density-functional theory (DFT) (Ref. 45) have been performed with the \textit{ab initio} full-potential augmented plane waves plus local orbitals (APW + \(lo\)) method\(^{46}\) as embodied in the WIEN2K code.\(^{47}\) Exchange and correlation effects were treated using the local spin density approximation (LSDA),\(^{48}\) the generalized-gradient approximation ([GGA], Ref. 49), and the Perdew-Burke-Ernzerhof parametrization of GGA for solids (PBE-sol) GGA.\(^{50}\)

In the APW + \(lo\) method the wave functions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radius \(R_{MT}\) and in plane waves in the remaining space of the unit cell (the interstitial region). The atomic sphere radii used for Zr, Ta, and O were 1.06, 1.06, and 0.90 Å, respectively. The parameter \(RK_{max}\), which controls the size of the basis set, was set to 6 (\(R\) is the smallest muffin-tin radius and \(K_{max}\) the largest wave number of the basis set) for the larger SCs and 8 in the case of the calculations performed in the undoped system. As stated in Ref. 4, zirconium is characterized by a strong overlap of the 4s, 4p, and 4d wave functions. For this reason we treat the Zr-4s, 4p, 4d, and 5s as valence electrons. To improve linearization, local orbitals\(^{47}\) were used to describe Zr-4p and 5s, Ta-6s, 5p, and 4f, and O-2s. Integration in reciprocal space was performed using the tetrahedron method taking up 50 \(k\) points in the full Brillouin zone (BZ), which are reduced to 14 \(k\) points in the irreducible wedge of the BZ (IWBZ). To plot the density of states (DOS), we calculated eigenvalues at a denser mesh.

In order to get the equilibrium structures, once self-consistency was achieved, quantum-mechanically-derived forces on the ions were obtained, then the ions were displaced according to a Newton-damped scheme, and the relaxed positions of the atoms were obtained (for details see Ref. 51 and references therein). This procedure was repeated until the forces on the ions were below a tolerance value of 0.01 eV/Å. Details of the calculation of the EFG within this code are described in the works of Schwarz et al.\(^{52}\)

To check the accuracy of the present results we performed several additional calculations. For selected systems, we varied the basis set from \(RK_{max} = 5.0\) to \(RK_{max} = 7.0\), and the
number of $k$ points from 50 to 200. Also we examined the effects of changing the muffin-tin radii on the properties of the system. Magnetic moments, electric field gradients, and interatomic distances can be obtained with adequate precision using $R_{\text{K}}_{\text{max}} = 6.0$ and 50 $k$ points (the interatomic distances, EFG components, and magnetic moments are converged to error bars smaller than 0.01 Å, $0.5 \times 10^{21}$ V/m$^2$, and 0.02 μB, respectively). We have also considered the inclusion of Zr-4$d$ and 4$s$ local orbitals. When these local orbitals are introduced no influence on the atomic forces was detected. The changes in the $V_{ii}$ components of the EFG at the Ta are smaller than $0.1 \times 10^{21}$ V/m$^2$.

Finally, and in order to check how the results depend on the lattice parameters we also performed calculations using $a$, $b$, $c$, and $\beta$ values reported by Hann et al. ($a = 5.15054$ Å, $b = 5.20314$ Å, $c = 5.31544$ Å, and $\beta = 99.1944.53$) The differences obtained in the equilibrium structures and hyperfine properties are within the convergence tolerance.

V. RESULTS AND DISCUSSION

A. Pure m-ZrO$_2$

In order to check the reliability of the theoretical approach, it was applied first to the pure system in order to analyze how well-established experimental results are reproduced. Therefore, before proceeding with the study of the doped system, a summary of the main results obtained for the pure system will be given in this section.

In these calculations, the lattice parameters were fixed at their experimental values, but the internal coordinates were optimized by force minimization. The resulting internal atomic positions and the distances from Zr to its oxygen nearest neighbors (ONN) are listed in Table I. As can be seen, the results obtained for the internal parameters $x$, $y$, $z$ using local density approximation (LDA), generalized gradient approximation (GGA), and PBE-sol are very similar and are in excellent agreement with the experimental results reported in the literature as well as previous calculations. The mean distance predicted by the three exchange and correlation potentials (LDA: 2.156 Å, GGA: 2.157 Å, PBE-sol: 2.157 Å) are also in good agreement with those determined by x-ray diffraction (XRD, 2.158 Å, Refs. 37 and 53) and extended x-ray absorption fine structure experiments (EXAFS, 2.16 Å, Ref. 54).

The density of states (DOS) of m-ZrO$_2$ is presented in Fig. 2. The overall band structure of pure m-ZrO$_2$ is consistent with previous works (see, for example, Refs. 5, 15, 55, 57, and 58) and the semiconducting nature of this material was found: There is a gap between the valence and the conduction bands, but the usual problem of the LDA gap underestimation is observed. The minimum gap predicted by LDA is 3.6 eV (the LDA band gap is smaller by about 0.1 eV than those obtained using GGA and PBE-sol), in good agreement with other calculations, whereas the experimental measured gap values are in the range 5.5–5.8 eV (Ref. 59) (a value of 5.0 eV was also reported). Electron energy-loss spectroscopy (EELS) revealed a low energy gap of zirconia of 3.8 eV that was attributed to defect states.

![FIG. 2. Total density of states of pure m-ZrO$_2$ (upper panel) and Zr-d and O-p partial DOS. Energies are referred to the valence-band maximum (labeled “$E_F$” here) shown by a vertical dotted line.](image-url)
value are found: A clear decrease in $\eta$ going from GGA to LDA and PBE-sol is observed. This difference in the $\eta$ values obtained by the approximations used for the exchange and correlation potential used here can be easily understood. In the case of the calculations using the experimentally determined internal coordinates $x$, $y$, and $z$, the calculations were performed with the same atomic positions, and very similar $\eta$ values were found in all the calculations but, in the case of the refined structures, slightly different equilibrium atomic positions were predicted. These results indicate that the different $\eta$ values obtained in this case can be related (due to the extreme sensitivity of the EFG to small changes in the local structure) to different equilibrium structures, as opposed to the different descriptions of the electronic structure of the undoped system. To support this we have carried out a series of calculations. We have taken the equilibrium structure predicted by GGA and, with these positions, we performed a calculation using PBE-sol, obtaining in this case $V_{ZZ} = +5.42 \times 10^{21} \text{V/m}^2$, $\eta = 0.11$, the same result obtained using the GGA parametrization. After that, we have taken the equilibrium structure predicted by LDA and performed GGA and PBE-sol calculations. We obtained a $V_{ZZ}$ value of about $+5.5 \times 10^{21} \text{V/m}^2$ and $\eta < 0.05$, the same results obtained in the LDA calculation. From these results we can conclude that, when we use the same structure LDA, GGA, and PBE-sol predict the same EFG tensor and, as a consequence, very similar electronic structures for $m$-$\text{ZrO}_2$.

The EFG can be determined with high accuracy and precision by means of hyperfine techniques. In this sense, one of the isotopes of Zr ($^{91}\text{Zr}$) can be used as a probe in NMR experiments and, in consequence, $^{91}\text{Zr}$ NMR spectroscopy is perhaps the most straightforward way to directly probe the nature of zirconium sites and learning about electronic and structural zirconium environments. However, $^{91}\text{Zr}$ NMR experiments in the solid state are notoriously difficult and challenging due to the low resonance frequency of $^{91}\text{Zr}$ and the relatively large $^{91}\text{Zr}$ nuclear quadrupole moment. For this reason, very few $^{91}\text{Zr}$ NMR studies in materials have so far been reported in the literature. In the case of $^{91}\text{Zr}$ NMR in $m$-$\text{ZrO}_2$, the spectrum is dominated by a pure quadrupolar interaction. The obtained results for $V_{ZZ}$ and $\eta$ are reported in Table II. The agreement between theory and experiment for $V_{ZZ}$ and $\eta$ is very good.

With these studies, we have demonstrated that APW $+lo$ correctly describes electronic, structural, and hyperfine properties of pure $m$-$\text{ZrO}_2$, giving us a solid basis to start the calculations for the Ta-doped system.

### Table II. Calculated and experimentally determined largest component of the diagonalized EFG tensor ($V_{ZZ}$) and asymmetry parameter $\eta$ at Zr sites in pure $m$-$\text{ZrO}_2$.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th>PBE-sol</th>
<th>Expt.</th>
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</thead>
<tbody>
<tr>
<td>$V_{ZZ}$</td>
<td>$\eta$</td>
<td>$V_{ZZ}$</td>
<td>$\eta$</td>
<td>$V_{ZZ}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Predicted equilibrium structures</td>
<td>+5.5</td>
<td>0.25</td>
<td>+5.4</td>
<td>0.24</td>
</tr>
<tr>
<td>$^{91}\text{Zr}$ NMR (Ref. 61)</td>
<td>+5.5</td>
<td>0.12</td>
<td>+5.4</td>
<td>0.04</td>
</tr>
<tr>
<td>Experimentally determined structure</td>
<td>5.52</td>
<td>0.25</td>
<td>5.5</td>
<td>0.12</td>
</tr>
</tbody>
</table>

#### B. $\text{Zr}_3\text{TaO}_{64}$

In order to analyze the effect of the inclusion of Ta impurities in the $m$-$\text{ZrO}_2$ host, the 96-atom SC was constructed and one of the Zr atoms was replaced by a Ta atom. In order to discuss the importance of the charge state of the impurity some preliminary calculations were performed. We calculated the self-consistent electronic structure of the 96-atom SC with all atoms in their initial unrelaxed positions in order to analyze the changes in the electronic structure of the system caused by the presence of the impurity, neglecting for the moment the problem of structural relaxations. The density of states of this system is presented in Fig. 3. Since the valence of Ta is 5+, when a Ta atom replaces a Zr$^{4+}$ atom in the SC, there is one electron in excess. Thus, the presence of the Ta impurity induces a partially filled impurity band at the bottom of the conduction band and the resulting system is metallic, as can be seen in Fig. 3. Note that the Ta $d$ band is described as very sharp peaks indicating that interaction between Ta atoms is quite small for this SC.

![FIG. 3. Total DOS of Ta-doped $m$-$\text{ZrO}_2$ and atom-resolved PDOS of Ta ($d$ contribution) and its ONN atoms ($p$ contribution) for the unrelaxed system $\text{Zr}_3\text{TaO}_{64}$. Energies are referred to the Fermi level ($E_F$).](image-url)
TABLE III. Relaxed bond lengths (in Å) from the Ta impurity to its seven ONN for Ta substitutionally replacing Zr in $m$-HfO$_2$ (Ref. 32 and 38), we performed calculations initially considering that the impurity level remains partially filled and the extra electron introduced into the host by the Ta atom remains localized close to this atom. In the framework of an ionic model, the Ta impurity is in a +4 state. We will call this state the neutral charge state or $q = 0$. Secondly, we assumed that the extra electron is removed from the impurity in some way. In this case the Ta impurity is in a +5 state, which in this text will be called charged state or $q = +1$. In order to maintain the neutrality of the system, the extraction of the electron is compensated in our calculations by a uniform background charge distribution.

For Ta-doped $m$-HfO$_2$, APW + lo calculations have predicted (and TDPAC experiments confirmed) that, depending on the charge state of the impurity, a local magnetic moment can appear. A similar result was obtained in other systems such as Cd complexes in Si and Ge. Based on these results spin-polarized calculations were performed. In the case of the charged cell ($q = +1$) we did not find a magnetic solution, while in contrast, APW + lo predicts spin polarization for the case $q = 0$. For this charge state, the three XC models predict a magnetic moment of 1.00 $\mu_B$. Total-energy calculations showed that the energy difference $\Delta E = E_{\text{sp}} - E_{\text{as}}$ is $-0.04$ eV ($E_{\text{sp}}$ and $E_{\text{as}}$ are the total energy of the spin-polarized and non-spin-polarized cases, respectively), showing that the spin-polarized cell is the energetically more stable. Similar results were obtained in the case of a larger SC.

The substitution of a Zr by a Ta atom in the $m$-ZrO$_2$ host is accompanied by a reconstruction of the positions of the surrounding atoms. In Table III we present the calculated results for the relaxed Ta-ONN bond lengths (since the results obtained using different approximations for the exchange and correlation potential are very similar, for the sake of simplicity we will present here and in the following only those obtained with GGA). It should be mentioned that for both charge states the amount of distortion per atom decreases rapidly from the oxygen nearest to the impurity to other shells. Similar to the case of $m$-HfO$_2$, a contraction of the Ta-ONN bond lengths was found for both charge states. As was expected, the Ta-ONN bond lengths strongly depend on the charge state.

<table>
<thead>
<tr>
<th>$d(Zr-O_{1a})$</th>
<th>$d(Zr-O_{1b})$</th>
<th>$d(Zr-O_{2a})$</th>
<th>$d(Zr-O_{2b})$</th>
<th>$d(Zr-O_{2c})$</th>
<th>$V_{ZZ}$</th>
<th>$\eta$</th>
<th>$B_{HF}$</th>
<th>$\mu^{SC}/\mu^{Ta_{aa}}$</th>
<th>$\Delta E = E^{sp} - E^{as}$</th>
</tr>
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<tbody>
<tr>
<td>Unrelaxed structure</td>
<td>LDA</td>
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<td>PBE-sol</td>
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<td>GGA</td>
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<td>2.08</td>
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<td>2.23</td>
<td>2.27</td>
<td>2.18</td>
<td>2.20</td>
</tr>
</tbody>
</table>

$V_{ZZ}$, in units of $10^{21}$ V/m$^2$, magnetic hyperfine field, $B_{HF}$ (in T), and asymmetry parameter $\eta$ at the Ta impurity site in $m$-ZrO$_2$ are also reported.
In Table IV, the results for the EFG tensor (major principal contributions to the EFG at Ta substitutional sites in m-ZrO₂, in units of 10⁻²¹ V/m², for the neutral (q = 0) and charged (q = +1) states of Ta in the system Zr₃TaO₆₄.

<table>
<thead>
<tr>
<th>Neutral cell (q = 0)</th>
<th>Charged cell (q = +1)</th>
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<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>q¹p</td>
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Contributions to the EFG

<table>
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<tr>
<th>Neutal cell (q = 0)</th>
<th>Charged cell (q = +1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vₓₓ</td>
<td>Vᵧᵧ</td>
</tr>
<tr>
<td>sd</td>
<td>+0.06</td>
</tr>
<tr>
<td>p</td>
<td>-2.8</td>
</tr>
<tr>
<td>d</td>
<td>-1.5</td>
</tr>
<tr>
<td>f</td>
<td>-0.08</td>
</tr>
<tr>
<td>total</td>
<td>-4.32</td>
</tr>
</tbody>
</table>

of the impurity. In effect, as can be seen in Table III, the magnitude of the contractions is larger in the case of q = +1. This is due to the change caused by the extra electron in the Coulomb interactions. The contractions of the Ta-ONN bond lengths can be understood from the fact that the bond lengths in tantalum oxide (TaO₂) are about 2.02 Å.

Regarding spin polarization, we found that the magnetic moments are independent of the structural distortion, i.e., a null magnetic moment was found for q = +1 and a magnetic moment of 1.00 μB/SC for q = 0. In this last case, spin polarization occurs mainly at the impurity sites (0.26 μB/Ta; see Table IV), while the remaining moment is almost uniformly distributed over the ONN atoms and the interstitial region. Similar to the case of the unreconstructed structures, after the structural relaxations the spin-polarized solution has lower energy (for the equilibrium structures Eₛₚ − Eₚₚ = −0.05 eV).

In the following the APW + lo results for the EFG tensor will be discussed and compared with the experimental ones. In Table III, the results for the EFG tensor (major principal component and asymmetry parameter) at the Ta site in the equilibrium structures obtained for the two charge states are given. In both cases, the differences between LDA, GGA, and PBE-sol are within the convergence tolerance. On the other hand, the difference in the EFGs obtained for the charged and neutral cells is remarkable and is not only caused by the different equilibrium structures. To understand the origin of this difference, we calculate the partial charges in the Ta muffin-tin sphere. It can be seen in Table IV that the population of the s and f states of Ta remains unaltered by the removal of one electron from the SC, while the population of the p and d orbital changes by +0.04 and -0.1 electrons from the neutral to the charged cells. Additionally, the local magnetic moment in the Ta sphere originates from the polarization of the d electrons.

In order to determine the effect of the charge difference between q = 0 and q = +1 on the EFG we focus on the valence contribution to the EFG which originates in the asymmetry of the valence charge distribution inside the muffin-tin sphere of the Ta atom. In the present case, the valence contribution is the dominant contribution and can be decomposed into the different orbital symmetries. As can be seen in Table IV the f and sd contributions to the EFG are negligible and nearly independent of the charge state of the impurity. But, the changes in the p and d populations produce drastic effects in the EFG. In the case of the neutral cell (impurity level partially occupied) the largest contribution to the EFG has it origin in the d electrons. When the impurity level is empty the d contributions drastically decrease, and the p contribution increases and becomes the dominant one. The role played by the charge state of the impurity on the symmetry of the electronic charge density can be better seen in Fig. 5. In this figure we present the atom-resolved partial density of states (PDOS) for the Ta atom in the relaxed structures of the 96-atom SC for both charge states of the impurity. As can be seen the impurity state at the Fermi level has important Ta dₓ²−₂ and Ta dₓ₂−₂ contributions, showing that even if small, the change in the population of the impurity state induces a drastic change in the symmetry of the charge distribution and, in consequence, of the EFG tensor.

C. Comparison with ¹⁸¹Ta TDPAC experiments

The TDPAC technique was extensively used to characterize Zr-based systems due to the easy incorporation of the well-known ¹⁸¹Ta probe since Hf is a natural impurity of Zr and the Ta probe is obtained from the nuclear reaction n + ¹⁸⁰Hf → ¹⁸¹Hf + β⁻ → ¹⁸¹Ta. In these experiments, the probe is extremely diluted (ppm). Under these conditions, phase transformations and chemical reactions were investigated following the EFG behavior. In the case of m-ZrO₂, the experimental results were generally analyzed with simple models that assume that the Ta impurity probe does not produce any structural or electronic perturbation of the host and the EFG is mainly caused by the host lattice (see, for example, Refs. 62 and 63).

In the TDPAC experiments two pure nuclear quadrupole interactions (NQI) were used to describe the TDPAC spectra (see Table V). The most populated one (in the following denoted HFI1) was associated with the defect-free regular cationic sites of the monoclinic phase (Vₓₓ = 14.054 × 10⁻²¹ V/m² and η = 0.335; Ref. 33). The second interaction (HFI2, characterized by Vᵧᵧ = 21.2 × 10⁻²¹ V/m² and η = 0.3–0.4), was tentatively associated with Ta at cationic sites with defects. Comparing the calculated EFG values of Table V and the experimental ones of Table III, it emerges that the agreement between theory and experiment is very good for both charge states, enabling us to unambiguously assign HFI1 to Ta in a regular cationic site of the monoclinic phase of m-ZrO₂ with the probe in a charged state. The other interaction also corresponds to a Ta atom in the cationic site but in this case the impurity energy level introduced by the Ta remains occupied by one electron. In other words, the Ta impurity acts as a trapping site.

Our calculations predict that, in the case of q = 0, the stable solution is the spin-polarized one. In consequence, HFI2 must have a combined quadrupole electric and dipolar magnetic character. Up to now, no evidence of this kind of interaction has been reported.
combined interaction was found in the literature for Ta-doped m-ZrO$_2$. When the perturbation is caused by a CEMI in addition to $V_{ZZ}$ and $\eta$, a magnetic frequency $\omega_L$ must be taken into account. Assuming that the second interaction is described by the predicted combined electric and magnetic interaction (hereafter denoted HFI2C), a new fit of the TDPAC experimental data obtained in coarse grained m-ZrO$_2$ (Ref. 33, with authors permission) was performed. Figure 6 shows the new fitted curve obtained by considering HFI2 as a CEMI hyperfine interaction. The obtained hyperfine parameters are summarized in Table V. The accuracy of the fit is comparable to that reported in Ref. 33. Independently of the model used for the second interaction, the fitted values corresponding to HFI1 remain unchanged. The other interaction (either HFI2 or HFI2C) represents mainly the anisotropy collapse of the TDPAC spectrum within a few nanoseconds, and in this way, it does not have enough structure to be unambiguously fitted. However, as it can be seen from Table V, HFI2 and HFI2C are characterized by very similar high $V_{ZZ}$ values. In the case of HFI2C a value of $\omega_L = 1071$ MHz was obtained from the fitting of the experimental TDPAC spectrum. With the use of Eq. (3) a magnetic hyperfine field $B_{HF} = 10.8$ T was derived, which is in good agreement with the calculated one ($B_{HF} = 9.2$ T). From all these results and the fact that APW + lo shows that the spin-polarized solution is energetically favorable, we conclude that the second interaction corresponds to Ta impurities located

![Diagram](image-url)

**FIG. 5.** (Color online) DOS of Ta-doped m-ZrO$_2$ (top), partial DOS of Ta $d$ characters (middle) and orbital-resolved partial DOS of Ta $d$ states (bottom). The results correspond to spin-polarized LDA calculations for the relaxed system $Zr_{31}Ta_{64}$ (96-atom SC) for $q = 0$ (left panels) and $q = +1$ (right panels). Energies are referred to the Fermi level ($E_F$). Note the change on the energy scale in the case of the orbital-resolved partial DOS of Ta $d$ states.

<table>
<thead>
<tr>
<th>Model for fitting</th>
<th>Interaction</th>
<th>Relative intensity (%)</th>
<th>$v_Q$</th>
<th>$V_{ZZ}$</th>
<th>$\eta$</th>
<th>$\Delta\delta/\delta$ (%)</th>
<th>$\omega_L$ (MHz)</th>
<th>$B_{HF}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure electric</td>
<td>HFI1</td>
<td>80</td>
<td>802$_2$</td>
<td>14.05$_5$</td>
<td>0.335$_5$</td>
<td>0.02$_1$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>quadrupolar (Ref. 33)</td>
<td>HFI2</td>
<td>20</td>
<td>1200$_{100}$</td>
<td>21$_{2}$</td>
<td>0.3-0.4</td>
<td>0.4$_{10}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CEMI</td>
<td>HFI1</td>
<td>53$_2$</td>
<td>808$_{5}$</td>
<td>14.16$_{4}$</td>
<td>0.33$_1$</td>
<td>0.03$_1$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(this work)</td>
<td>HFI2C</td>
<td>47$_2$</td>
<td>1200$_{6}$</td>
<td>21.0$_{1}$</td>
<td>0.46$_{1}$</td>
<td>0.01$_{1}$</td>
<td>107$_1$</td>
<td>10.8$_{3}$</td>
</tr>
</tbody>
</table>

**TABLE V.** Nuclear coupling constant frequency $v_Q$ (in MHz), electric field gradient main component $V_{ZZ}$ (in units of $10^{21}$ V/m$^2$), asymmetry parameter $\eta$, relative frequency distribution ($\Delta\delta/\delta$), precession frequency $\omega_L$ (in MHz), and magnetic hyperfine field $B_{HF}$ (in T) characterizing the hyperfine interactions observed in TDPAC experiments in m-ZrO$_2$ (Ref. 33). In order to calculate $V_{ZZ}$ from $v_Q$ we used Eq. (1) and $Q^{(181}Ta) = 2.36$_b (Ref. 40). $B_{HF}$ was obtained from $\omega_L$ using Eq. (3).
Concerning hyperfine parameters, the present calculations show that the experimentally determined hyperfine interactions can be attributed to two different coexisting charge states of the Ta impurity probe atom. In the case of the \( q = 0 \) charge state (this charge state corresponds to the trapping of one electron by the Ta impurity), our calculations predict that the lowest energy solution corresponds to a spin-polarized state with a net magnetic moment of 1.0 \( \mu_B/\text{SC} \) (0.26 \( \mu_B \) in the Ta muffin-tin sphere). A new analysis of the TDPAC results supports this prediction.

The pronounced dependence of the hyperfine properties on the charge state of the impurity can be explained by analyzing the electronic structure of the defect zirconia. The difference in the EFG in magnitude and symmetry between the charged and neutral states of the impurity arises from the filling of the impurity level at the Fermi energy, mainly composed by \( d_{x^2-y^2} \) levels. In consequence, the population/depopulation of this impurity level produces a drastic change in the symmetry of the charge density distribution in the close vicinity of the Ta probe atom. For this reason, the removal of one electron from the cell produces a change in the Coulomb repulsion (this is the reason for the different structural distortions predicted for each charge state) and a pronounced change in the hyperfine properties (due to the change of the symmetry of the charge distribution).

It is interesting to note that the calculated EFGs at Ta impurities substitutionally located at cationic sites in \( m\)-\( ZrO_2 \) are very similar to those previously found in Ta-doped \( m\)-\( HfO_2 \). This result (in perfect agreement with the experiments) shows that the effect of the second neighbors (Zr or Hf) on the charge distribution near Ta is negligible. To check this assertion we investigated the different contributions to the EFG, and found that the valence contribution (those originating from the nonspherical electron density of the valence and semicore electrons within the Ta muffin-tin sphere) dominates, while the lattice term is almost negligible. The valence contribution can be further decomposed according to the different orbital symmetries. In the case of \( q = 0 \) the main contribution comes from the \( d \) states, while in the case of \( q = +1 \) the EFG have essentially \( p \) character. This analysis also shows that the magnetic moment in the Ta muffin-tin sphere is predominantly due to polarization of the \( d \) electrons.

From our results it is clear that the Ta impurity heavily perturbs the \( m\)-\( ZrO_2 \) host, and that the hyperfine interactions (EFG, BHF) strongly depend on and are closely related to the electronic and structural effects induced by the impurity atom. In consequence, the impurity character of the probe and the effects that it induces in the host must be taken into account to obtain a proper description of the system.

**ACKNOWLEDGMENTS**

This work was partially supported by UNNOBA, Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) under Grant No. PICT98 03-03727, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) under Grants No. PE16174 and No. PIP6032, Fundación/Antorchas, Argentina, and the Third World Academy of Sciences.
(TWAS), Italy, under Grant No. RGA 97-057. This research made use of the HP-Parallel-Computing Bose Cluster and the computational facilities at IFLP and Departamento de Física (UNLP). The authors thank M. Forker for fruitful discussion and for permitting us to use TDPAC experimental results.

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PHYSICAL REVIEW B 85, 155202 (2012)