I. INTRODUCTION

Hafnium dioxide has attracted much attention due to its potential technological applications. HfO$_2$ is a wide-bandgap semiconductor that crystallizes in a monoclinic structure (m-HfO$_2$) at room temperature. It transforms to a tetragonal structure at moderately elevated temperatures and to a cubic structure at higher temperatures. HfO$_2$ is characterized by a high melting point, high chemical stability, and a large dielectric constant. In its various forms and with the addition of small amounts of impurities, it has applications ranging from solid oxide fuel cell electrolytes to catalyst substrates, and protective coatings (see Ref. 1 and references therein). More recently, ferromagnetism was observed in pure HfO$_2$ thin films, a result of interest to the field of spintronics.$^2$

Time differential perturbed angular correlation (TDPAC) spectroscopy is a powerful technique to study hafnium compounds. To perform a TDPAC experiment, a suitable probe isotope (generally an impurity) must be introduced adequately in the system under study. In the case of Hf compounds, the $^{181}$Hf($^{181}$Ta) probe can be obtained by neutron irradiation of the naturally occurring $^{180}$Hf isotope. The small [parts per million (ppm)] concentration of radioactive tracer atoms necessary to perform the experiment does not influence the macroscopic properties of the matrix. Additionally, in comparison with other nuclear techniques such as Mössbauer spectroscopy, the sensitivity of TDPAC does not depend on a Debye-Waller factor allowing to determine properties or effects occurring at high temperatures. For these reasons, HfO$_2$ has been extensively studied by means of TDPAC.$^3$

The TDPAC technique provides a high-resolution determination of quadrupolar electric, dipolar magnetic hyperfine interactions, or a combination of both.$^4$ The electric quadrupolar interaction is essentially given by the product of the nuclear quadrupole moment, $Q$, characteristic of a given nuclear state of spin $I$, and the electric field gradient (EFG) at the nuclear site. $Q$ is 2.36$_5$ b for the sensitive TDPAC state of $^{181}$Ta.$^5$ The measured quantity is the nuclear quadrupolar frequency $\omega_Q$, which is given by $\omega_Q = eQV_{ZZ}/\{4I(2I-1)\hbar\}$, where $V_{ZZ}$ is the major component of the diagonalized EFG tensor. The EFG tensor is completely specified by $V_{ZZ}$, together with the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$. 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.$^4$ The experimentally observed quantity is in this case the precession frequency $\omega_L = g_e\mu_B|B_M|/\hbar$, where $g_e$ denotes the nuclear $g$ factor and $\mu_B$ is the nuclear magneton.$^6$ $B_M$ is the magnetic hyperfine field, which is a fingerprint of the magnetic configuration and the spin polarization near and at the probe nucleus. Whereas pure quadrupolar and/or pure magnetic interactions have been extensively observed using TDPAC, cases of combined electric and magnetic interactions (CEMIs) in which the quadrupolar electric and the dipolar magnetic interactions are of the same order of magnitude are scarce in the literature.$^7,8$ In the case of a CEMI, the experimentally observed parameters are the quadrupole frequency $\omega_Q$, 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.

All published TDPAC studies of Ta-doped m-HfO$_2$ reported in the literature refer to a hyperfine interaction (HF1) characterized by a $V_{ZZ}$ of about $13.7 \times 10^{11}$ V/m$^2$ and an asymmetry parameter $\eta$ of about 0.35 at 300 K.$^9$ This interaction was assigned to $^{181}$Hf($^{181}$Ta) substitutionally located at the cation sites of $m$-HfO$_2$. An ab initio study on
Ta-doped \( m \)-HfO\(_2\) performed in Ref. 1 showed that Ta atoms induce a donor impurity level close to the conduction band of \( m \)-HfO\(_2\). By comparing the calculated EFG values with the experimental results it was confirmed that HfI1 corresponds to Ta probes located at cationic sites and that the impurity level is ionized (empty) at 300 K.

The experimental results showed that, in addition to HfI1, there exist a second interaction in \( m \)-HfO\(_2\). Ayala et al.\(^9\) reported a second interaction in coarse grained \( m \)-HfO\(_2\) characterized by high \( V_{ZZ} \) and \( \eta \) values. Forker et al.\(^2\) investigated the structure, phase transformations, grain growth, and defects of coarse-grained and bare nanoparticles of \( m \)-HfO\(_2\) synthesized in a microwave plasma. The authors found that, in addition to the well-known HfI1, a second component involving 20–30% of the probe nuclei appeared in the \(^{181}\)Ta PAC spectra. The fitted parameters are similar to those reported in Ref. 9. The temperature dependence of this component was reproduced by assuming that Ta impurities in hafnia may trap electrons at low temperatures. This second interaction (hereafter denoted HfI2) was never assigned to a regular crystallographic site.

In order to understand the origin of HfI2 we performed in this work a detailed study of the electronic and structural properties of Ta-doped HfO\(_2\) for different charge states of the impurity-host system. Since \textit{ab initio} calculations showed that impurities can leave unpaired electrons that can lead to a net magnetic moment,\(^10\) spin-polarized calculations were carried out. The theoretical predictions were compared with a new analysis of the TDPAC experiments reported in Ref. 3.

\section{II. METHOD OF CALCULATION}

The calculations were performed with the \textit{ab initio} full-potential linear augmented plane wave plus local orbital (APW+lo) method\(^11\) in a scalar relativistic version, as implemented in the WIEN2K code.\(^12\) For the simulation of the diluted Ta impurity, the supercell (SC) scheme was employed following the general guidelines of our previous work.\(^1\) Calculations were made for a periodic arrangement of eight unit cells of \( m \)-HfO\(_2\). The resulting 96-atom SC has dimensions \( a'=2a=10.234 \text{ Å} \), \( b'=2b=10.3508 \text{ Å} \), and \( c'=2c=10.583 \text{ Å} \). One Hf atom of the SC was replaced by one Ta atom. With this arrangement, Ta substitution represents about 3 at. % doping. Although this Ta concentration is large compared with parts per million dilution 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 between impurities. In some cases calculations were performed using cells with 192 atoms (\( a'=2a=10.234 \text{ Å} \), \( b'=2b=10.3508 \text{ Å} \), and \( c'=4c=21.166 \text{ Å} \)) and 324 atoms (\( a'=3a=15.351 \text{ Å} \), \( b'=3b=15.5262 \text{ Å} \), and \( c'=3c=15.8745 \text{ Å} \)), respectively. The 324 atom SC is the largest SC we could use, maintaining the accuracy of the calculations.

In all cases we used the local spin-density approximation (LSDA, Ref. 13) and the exchange-correlation potential given by Wu and Cohen.\(^14\) The energy cut-off criterion was \( R_{\text{MT}}K_{\text{MAX}}=7 \) (\( R_{\text{MT}}K_{\text{MAX}}=6 \) for the 324-atom SC), \( R_{\text{MT}} \) being the smallest muffin-tin radius and \( K_{\text{MAX}} \) the largest wave number of the basis set. The number of \( k \) points was increased up to 100 to check the convergence of the results. Bond lengths, EFG components, and energy differences between spin-polarized and nonspin-polarized calculations are well converged for the employed parameters. Details of the calculation of the EFG within this code are described in the works of Schwarz et al.\(^15\) Relaxation of all the internal atomic positions, that is, the displacements of all the atoms in the SCs were considered.

As shown in a previous work,\(^1\) the presence of the Ta impurity induces a partially filled impurity band at the bottom of the conduction band. These impurity states are spatially located at the Ta atom and its oxygen nearest neighbor (Omn). As it was demonstrated in Refs. 1, 16, and 17, the charge state of the impurity can modify the electronic structure around the impurity. This change can strongly affect the structural distortions and the EFG. In a first scenario, it was assumed that a neutral Ta substitutes Hf in \( m \)-HfO\(_2\) and remains in a +4 valence state (henceforth “neutral charge state,” \( q=0 \)). In this case, the impurity state located at the Fermi levels are partially occupied (see Ref. 1). Secondly, calculations removing one electron from the whole system (\( q=+1 \)) were performed, this case is referred to as “charged state” in which the impurity state is empty. The charge imbalance is compensated by adding a uniformly distributed charge of opposite sign in the SC.

\section{III. RESULTS AND DISCUSSION}

In Table I we present the calculated results for the relaxed Ta-Omn bond lengths and for the EFG at the Ta site. Comparing the new results with those reported in Ref. 1, it can be seen that the effect of the relaxation of the second and further neighbors do not affect significantly neither the Ta-Omn bond lengths nor the EFG.

Table II shows the experimental values of the hyperfine parameters reported in Ref. 3. Comparing the calculated EFG values of Table I and the experimental ones of Table II, it can be seen that the agreement theory-experiment is remarkable for both charge states. As it was discussed in Ref. 1, HfI1 is related to Ta in a regular cationic site of the monoclinic phase with the probe in a charged state. The other interaction also corresponds to a Ta 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. Coexistence of different charge states was also found for Cd impurities in oxides by a combined TDPAC experimental and \textit{ab initio} theoretical study of Cd-doped SnO (Ref. 18) and in TiO\(_2\)–\(^{19}\). This indicates that the coexistence of different charge states in doped or nonstoichiometric oxides may be rather usual.

For some systems (such as Cd complexes in Si and Ge) calculations performed with the Korringa-Kohn-Rostoker-Green’s-function approach have predicted a local magnetic moment that depends on the charge state of the impurity.\(^10\) In effect, in a simple picture, a magnetic signal could be observed whenever a localized state is occupied by a single electron. Therefore, we performed spin-polarized calculations in the 96-atom SC for both charge states. In the case of
the charged cell ($q=+1$) there is an even number of electrons while the neutral cell has an odd number of electrons. Thus, in principle, this last case should be the better candidate to present magnetism due to the possibility of an unpaired spin moment. The results of the spin-polarized calculations are shown in Table III. In the case of the charged cell we did not find a magnetic solution, while in contrast, APW+$lo$ predicts a net magnetic moment of 1.0 $\mu_B$ for the spin-polarized case by −0.13 eV compared with the nonspin-polarized solution for $q=0$. The results obtained for $V_{ZZ}$ and $\eta$ for both SCs are shown in Table III. As expected, the hyperfine parameters are very similar to those determined for the 96-atom SC.\footnote{Ref. 3} Again, a net magnetic moment of 1.0 $\mu_B$ (0.35 $\mu_B$ in the Ta muffin-tin sphere) was found for $q=0$. The energy difference between spin-polarized and nonspin-polarized calculations favored the spin-polarized case by −0.13 eV (192-atom SC) and −0.12 eV (324-atom SC).

The present calculations show that the experimentally determined hyperfine interactions can be attributed to two different charge states of the probe atom. Moreover, HFI2 could have a combined quadrupole electric and dipolar magnetic character. Up to now, no evidence of this kind of combined interaction was found in the literature for Ta-doped HfO$_2$. When the perturbation is caused by a CEMI in addition to a net magnetic moment of 1.0 $\mu_B$ the second interaction is described as $HFI_2C$ (Ref. 3). Assuming that the second interaction is described by the predicted combined electric and magnetic interaction (hereafter denoted HFI2C), a new fit was performed on an

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### Table I. Final distances (Å) from the Ta impurity to its seven O neighbors for the different calculations

<table>
<thead>
<tr>
<th>$d$(Ta-Ox)</th>
<th>Unrelaxed structure</th>
<th>LDA</th>
<th>GGA</th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$(Ta-O1)</td>
<td>2.03</td>
<td>1.99</td>
<td>2.00</td>
<td>1.95</td>
<td>1.96</td>
</tr>
<tr>
<td>$d$(Ta-O2)</td>
<td>2.07</td>
<td>2.02</td>
<td>2.02</td>
<td>1.97</td>
<td>1.98</td>
</tr>
<tr>
<td>$d$(Ta-O3)</td>
<td>2.13</td>
<td>2.06</td>
<td>2.05</td>
<td>2.06</td>
<td>2.06</td>
</tr>
<tr>
<td>$d$(Ta-O4)</td>
<td>2.14</td>
<td>2.11</td>
<td>2.11</td>
<td>2.06</td>
<td>2.07</td>
</tr>
<tr>
<td>$d$(Ta-O5)</td>
<td>2.17</td>
<td>2.12</td>
<td>2.11</td>
<td>2.07</td>
<td>2.08</td>
</tr>
<tr>
<td>$d$(Ta-O6)</td>
<td>2.23</td>
<td>2.19</td>
<td>2.20</td>
<td>2.18</td>
<td>2.17</td>
</tr>
<tr>
<td>$d$(Ta-O7)</td>
<td>2.25</td>
<td>2.20</td>
<td>2.20</td>
<td>2.19</td>
<td>2.18</td>
</tr>
</tbody>
</table>

$V_{ZZ}(Ta Site)$: +20.0 | +21.4 | +13.7 | +13.9

$\eta(Ta Site)$: 0.42 | 0.40 | 0.33 | 0.30

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### Table II. Electric field gradient main component $V_{ZZ}$, asymmetry parameter $\eta$, relative frequency distribution $\Delta \delta/\delta$, and magnetic hyperfine field, $B_{hf}$, characterizing the hyperfine interaction observed in TDPAC experiments in $m$-HfO$_2$ (Ref. 3). In order to derive $V_{ZZ}$ from $\omega_{d}$ we used the value $Q(Ce^{185}Ta) =2.36_{8}$ b (Ref. 5).

<table>
<thead>
<tr>
<th>Model for fitting</th>
<th>Interaction</th>
<th>Relative intensity (%)</th>
<th>$V_{ZZ}$ ($10^{21}$ V/m$^2$)</th>
<th>$\eta$ (%)</th>
<th>$\Delta \delta/\delta$ (%)</th>
<th>$B_{hf}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure electric quadrupolar (Ref. 3)</td>
<td>HFI1</td>
<td>75</td>
<td>13.90$_{4}$</td>
<td>0.345$_{5}$</td>
<td>7$_{1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HFI2</td>
<td>25</td>
<td>23$_{2}$</td>
<td>0.3–0.4</td>
<td>40$_{10}$</td>
<td></td>
</tr>
<tr>
<td>CEMI (this work)</td>
<td>HFI1</td>
<td>82</td>
<td>13.56$_{2}$</td>
<td>0.36$_{1}$</td>
<td>6$_{1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HFI2C</td>
<td>18</td>
<td>22.7$_{3}$</td>
<td>0.47$_{2}$</td>
<td>1$_{1}$</td>
<td>11.2$_{3}$</td>
</tr>
</tbody>
</table>
The experimental TDPAC spectrum at room temperature, which was previously measured in coarse-grained HfO$_2$ (Ref. 3, with author permission) shows the new fitted curve obtained by considering a CEMI. The obtained hyperfine parameters are summarized in Table II and compared with those reported in Ref. 3 for the case of two pure electric quadrupole interactions. The accuracy of the fit is comparable to that reported in Ref. 3. Independently of the model used for the second interaction, the fitted values corresponding to HFI$_1$ remain unchanged. The other interaction (either HFI$_2$ or HFI$_2C$) represents mainly the anisotropy collapse of the TDPAC spectrum within a few nanoseconds, and in this way, it has not enough structure to be unambiguously fitted. However, as it can be seen from Table II, HFI$_2$ and HFI$_2C$ are characterized by very similar high $V_{ZZ}$ values.

Regarding the EFG, HFI$_2$, and HFI$_2C$ are in agreement with our APW+$lo$ prediction for both the nonspin-polarized and the spin-polarized calculations performed for the neutral charge state (see Table III). In the case of HFI$_2C$, from the magnetic frequency $\omega_L = g_N\mu_B B_{hf}/\hbar$ a magnetic hyperfine field of $B_{hf} = 11.2$ T is derived, which is in excellent agreement with the calculated one ($B_{hf}^{calc} = 11.8$ T). From all these results and the fact that APW+$lo$ predicts that the spin-polarized solution is energetically favorable, we conclude that the second interaction corresponds to Ta impurities probes located at Hf sites in a neutral charge state $q = 0$ with a net magnetic moment of about 0.35 $\mu_B$ in the Ta sphere.

As already mentioned, some authors have reported ferromagnetism in pure HfO$_2$ thin films. In some papers the observed magnetism was associated with iron impurities while in others its origin was attributed to intrinsic defects of the material. One possible mechanism proposed for the observed magnetism is related to native oxygen vacancies, which act as donors, leading to the $n$-type doping of the material. However, in this case the magnetic interaction is negligible, and this rules out that hypothesis. In contrast, Hf vacancies show a high-spin state with an associated magnetic moment of about 3.5 $\mu_B$. However, other groups argue that the hafnium vacancies are less likely to occur than the oxygen vacancies due to the high charge state. It is also found that most of the ferromagnetism in HfO$_2$ is induced by the surface or the interface with the substrates instead of the bulk. The present calculation and the new interpretation of the experimental results indicate that the trapping of an electron at a cationic site can induce a magnetic moment local-
ized at this site. This trapping effect could be related to the magnetism observed in thin films of pure HfO$_2$ since the surfaces could act as trapping centers. Further experiments and calculations will be very valuable in order to determine a possible magnetic ordering and the mechanism (or conditions) involved in a possible ferromagnetic behavior of HfO$_2$.

### IV. SUMMARY AND CONCLUSIONS

Density-functional calculations of the electronic structure and atomic forces have been used to examine monoclinic Ta-doped m-HfO$_2$ including spin-polarized calculations for different charge states. The force calculations were applied to optimize the doped structures relaxing all the atomic positions in the SC approximation. From the self-consistent potentials, hyperfine parameters at the Ta site were derived. The results were compared to the experimental TDPAC results reported in the literature and a new analysis of previous experimental results was performed.

The two experimentally detected hyperfine interactions were explained in terms of two different coexisting charge states for the Ta probe atom, giving an interpretation of the second hyperfine interaction at the Ta probe as originating from the $q=0$ charge state. This charge state corresponds to the trapping of one electron by the Ta impurity. In this charge state, the APW+lo calculations predict a net magnetic moment of 1.0 $\mu_B$ in the SC (0.35 $\mu_B$ in the Ta muffin-tin sphere).

The results of the TDPAC experiments are compatible with the presence of a combined quadrupolar electrical +dipolar magnetic interactions. An excellent agreement between the experimental and theoretical magnetic hyperfine fields was obtained.

### ACKNOWLEDGMENTS

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