



# Magnetic solution in Ta-doped monoclinic HfO<sub>2</sub>

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## HfO<sub>2</sub>

- Wide band gap (5.68 eV ) semiconductor
- High melting point
- High chemical stability
- Large dielectric constant
- Similar to ZrO<sub>2</sub>

With the addition of small amount of impurities it has industrial applications:

- Solid fuel cell electrolytes
- Catalyst substrates
- Protective coatings

-In the last years,  $\text{HfO}_2$  has attracted much research attention because of its potential application as an alternative to  $\text{SiO}_2$  as a dielectric in microelectronic devices due to these properties and stability on Si.

-Recently, **ferromagnetism was discovered in pure  $\text{HfO}_2$  thin films**

Different mechanisms were proposed in order to explain the observed ferromagnetism:

- O and Hf vacancies
- Effects of the surface
- Effects of the interface with the substrate

HfO<sub>2</sub> has monoclinic structure

$a = 5.1170_1 \text{ \AA}$ ,  $b = 5.1754_2 \text{ \AA}$ ,  $c = 5.2915_2 \text{ \AA}$

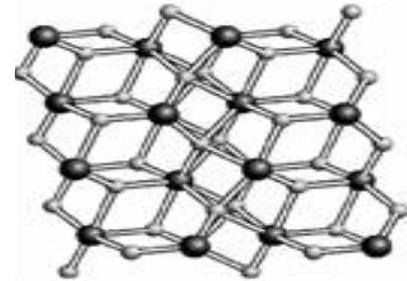
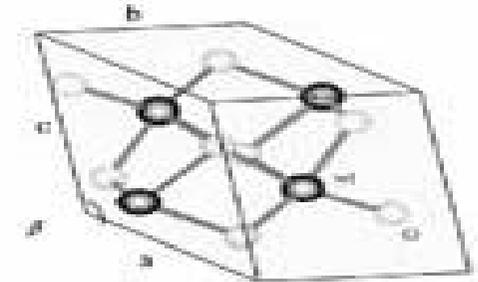
$\beta = 99.216_2$

-The unit cell contains 4 Hf atoms and 8 O atoms  
at general positions of C<sub>2h</sub>5 (P21/c):

(4c)  $(x,y,z; -x,y+1/2, 1/2-z)$ .

- The Hf atoms exhibit a sevenfold coordination with Hf-O distance between 2.04 Å and 2.26 Å.

- There are two kinds O that are differently coordinated, O(1) having three Hf neighbors at 2.04 – 2.15 Å and O(2) having 4 Hf at 2.16-2.26 Å.





## Impurities, defects or surfaces and interfaces can introduce

- Local structural distortions in the host lattice
- Impurity levels in the gap of the semi-conductor, modifying the electronic structure of the system.

## One way to measure electronic properties on an atomic scale is to use hyperfine experimental techniques

- Nuclear Quadrupole Resonance (NQR)
- Nuclear Magnetic Resonance (NMR)
- Mössbauer Spectroscopy (MS)
- Time Dependent Perturbed Angular Correlations (TDPAC)

- 
- TDPAC provides a high resolution determination of the electric-field-gradient (EFG) tensor at the site of a probe-atom (generally an impurity in the system under study), a quantity particularly sensitive to slight local changes in the asymmetry of the electronic charge density around the (impurity)-probe.
  - The measured EFG may give structural and electronic information of the system that cannot be obtained by other methods.
  - The interpretation of such experiments is not straightforward. In fact, interpretation of experimental EFG results involves understanding of chemical differences between the probe atom and the ion replaced by the impurity.
  - The experimental results show that the differences between probes and indigenous atoms are manifest in subtle ways that are not well described by simple models

## TDPAC results

- 1- Experiments were performed with  $^{181}\text{Ta}$  as probe atom
- 2- Probe atoms remain in a very dilute proportion (ppm)
- 3- It is assumed that probes occupies the cation site
- 4-  $^{181}\text{Ta}$  is obtained from neutron capture of the indigenous  $^{180}\text{Hf}$
- 5- The measurements are performed by measuring the delay time between two gamma rays. This cascade of rays is produced **after a beta-minus decay** of the excited nucleus.
- 6- The observed EFG is determined from the Quadrupolar Interaction (QI) of the EFG at the probe site and the quadrupole moment on Ta, not on Hf.

6- Chemically Hf acts as a +4 cation in the host.

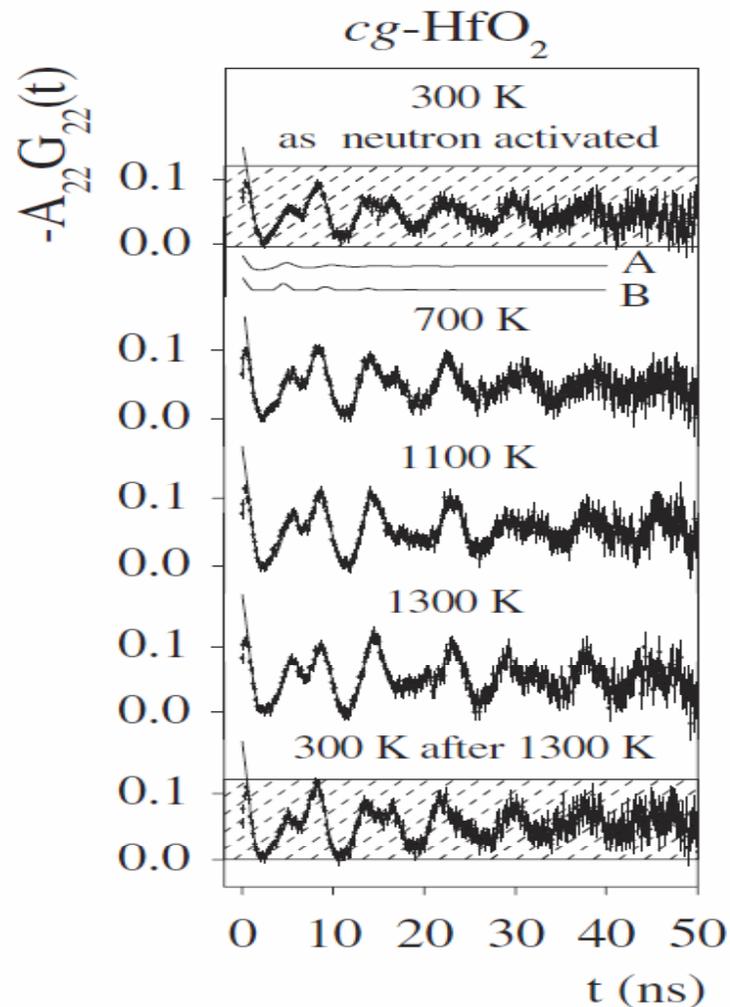
7- Chemically the Ta probe acts as a donor impurity, but its charge state is not a priori known.

8- If for some reason, the charge distribution around the probe is varying in time during the radioactive cascade, a dynamic quadrupole interaction will take place. This can occur if probe is changing the charge state, moving H inside the samples, etc.

$$V_{i,j}(\vec{r} = 0) = \frac{\partial^2 V}{\partial x_i \partial x_j} \Big|_{\vec{r}=0}$$

The eigenvalues of the EFG tensor are denoted  $V_{xx}$ ,  $V_{yy}$ , and  $V_{zz}$ , and the conventional choice is  $|V_{xx}| \leq |V_{yy}| < |V_{zz}|$ . Hence,  $V_{zz}$  is the largest eigenvalue of the EFG tensor, and the asymmetry parameter  $\eta$  is a measure of the difference between the two eigenvalues  $V_{xx}$  and  $V_{yy}$ :

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$



Two different QI interactions were observed:

PHYSICAL REVIEW B 78, 165206 2008

TABLE I. The QI parameters ( $\nu_q$ ,  $\eta$ , and  $\delta$ ) and the relative intensities of the two components present in the PAC spectra of  $^{181}\text{Ta}$  in coarse-grained  $\text{HfO}_2$  and  $\text{ZrO}_2$  at 300 K.

Component	Relative intensity	$\nu_q$ (MHz)	$\eta$	$\delta$
<i>cg-HfO<sub>2</sub></i>				
I-monoclinic	0.75	793(2)	0.345(5)	0.07(1)
II-QI distribution (A)	0.25	1300(100)	0.3–0.4	0.4(10)

↕  
Not so far analyzed at present

FIG. 5. PAC spectra of  $^{181}\text{Ta}$  in powder samples (in vacuum) of coarse-grained  $\text{HfO}_2$  (left-hand column) and  $\text{ZrO}_2$  (right-hand column) at different temperatures. The solid lines below the topmost spectra represent the perturbation factor of the disordered component; curves A for a static QI distribution; curve B for a slowly fluctuating QI. The height of the striped areas is a measure of the monoclinic fraction at 300 K after the samples passed through 1300 and 1530 K, respectively.

PHYSICAL REVIEW B 77, 054108 (2008)

## Method of Calculation

- DFT
- WIEN2k implementation of the APW+LO
- GGA and LDA approximations
- Pure HfO<sub>2</sub>
- Hf<sub>0.75</sub>Ta<sub>0.25</sub>O<sub>2</sub>
- Supercell calculations 2x2x2 (96 atoms Hf<sub>0.97</sub>Ta<sub>0.03</sub>O<sub>2</sub> with a separation between Ta atoms = ~10.3 Å) and tests on 3x3x3
- Tests on calculus convergence
- Relaxation of the inner atomic coordinates of the whole cell (Newton-damped until forces < 0.01 eV/Å)
- Tests with different charge states of the impurity
- Calculation of the EFG at Ta sites
- Comparison with experiment

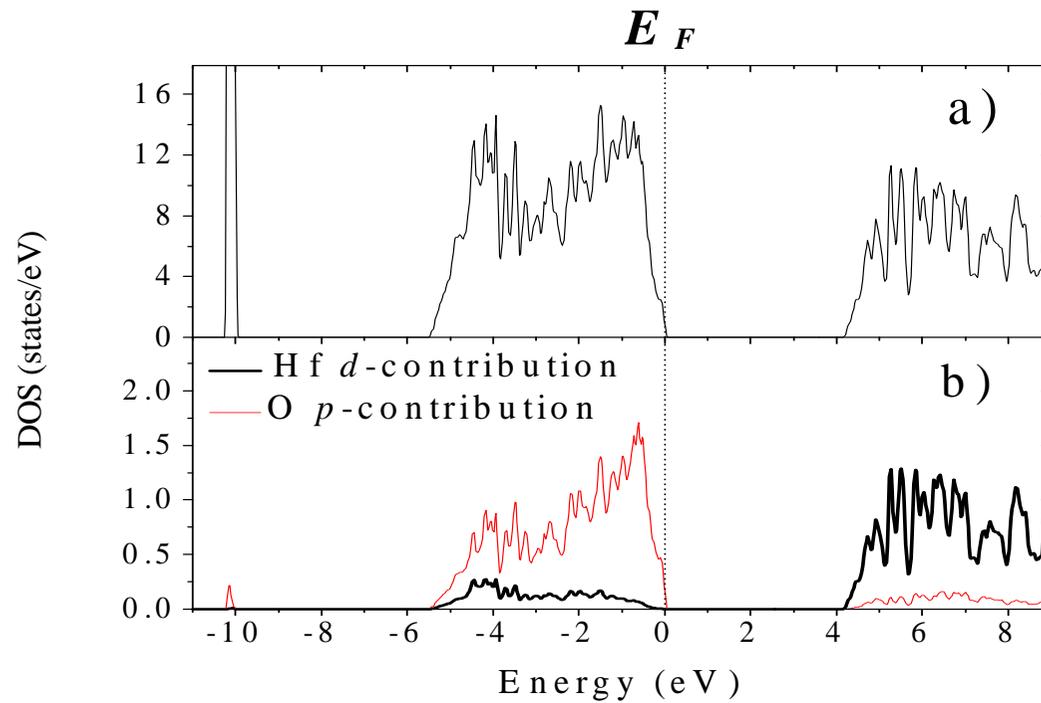
# Pure HfO<sub>2</sub>

a= 5.115 b=5.1754 c= 5.2915 B= 99.216

Atom	LDA calculation	GGA calculation	Exp.
x(Hf)	0.277	0.276	0.2755 <sub>2</sub>
y(Hf)	0.041	0.042	0.0397 <sub>1</sub>
z(Hf)	0.208	0.208	0.2080 <sub>2</sub>
x(O1)	0.070	0.069	0.0739 <sub>20</sub>
y(O1)	0.334	0.330	0.3318 <sub>17</sub>
z(O1)	0.343	0.345	0.3466 <sub>17</sub>
x(O2)	0.449	0.4445	0.4489 <sub>20</sub>
y(O2)	0.758	0.758	0.7582 <sub>16</sub>
z(O2)	0.479	0.478	0.4800 <sub>22</sub>

-Lattice parameters at exp. Values.

-Very good agreement with both LDA and GGA with exp.



- Indirect gap of about 4.1 eV
- 1.6 eV smaller than photoemission exp. (5.68 eV)
- Two valence band:
  - 1 narrow lower band at -10 eV mainly O-2s states
  - 2 upper -6.0  $\rightarrow$  0 eV mainly O-2p and Hf-5d
- Conduction band mainly Hf-5d and O-2p

	LDA calculation		GGA calculation	
	$V_{ZZ} * 10^{21} \text{ V/m}^2$	$\eta$	$V_{ZZ} * 10^{21} \text{ V/m}^2$	$\eta$
Experimental structural parameters	+11.6	0.53	+11.7	0.54
Predicted equilibrium structures	+12.6	0.11	+12.2	0.38
Inverting final relaxed atomic positions LDA<->GGA	+12.5 (GGA calc.)	0.10	+12.0 (LDA calc.)	0.39

-No experimental values of the EFG in the pure oxide

-Max difference between EFG for the experimental and calculated internal coordinates 10% for the principal component  $V_{zz}$ .

- No difference in the results between LDA and GGA approximations.

-The difference between the EFG predicted by LDA and GGA comes from the tiny differences in the relaxed positions.

-Small changes in the atomic positions produce large changes in the EFG tensor.

# TaHf<sub>3</sub>O<sub>8</sub>

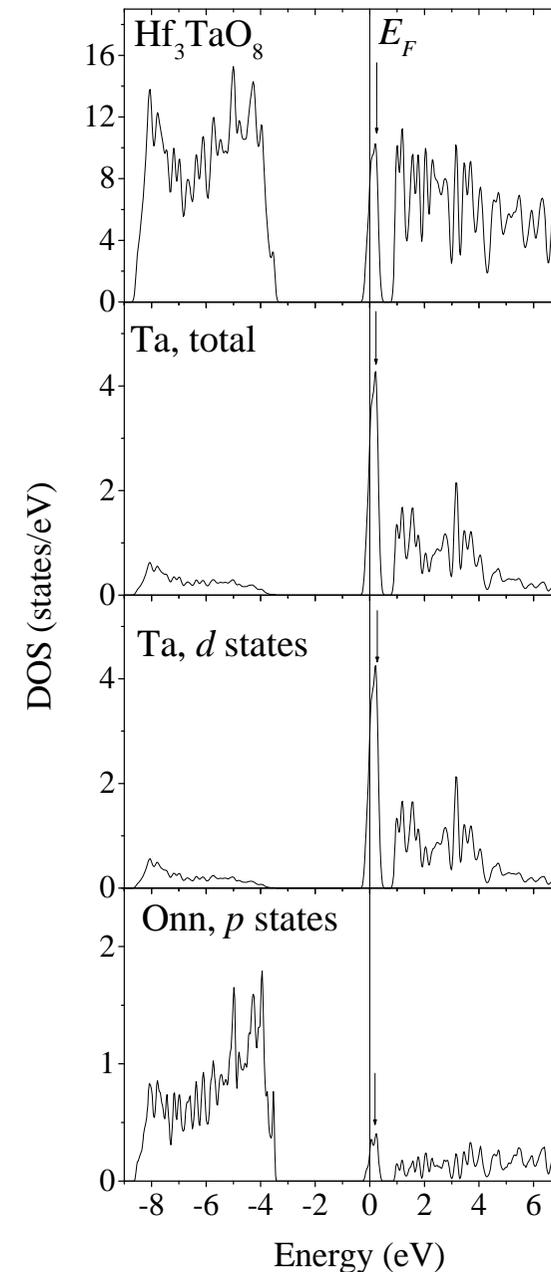
-Since the Ta valence is 5+, when a Ta atom replaces Hf, the resulting system is metallic.

-the presence of the Ta impurity induces an impurity band, partially filled, at the bottom of the conduction band

-The impurity state has mainly Ta- $d_z^2$  and Ta- $d_{x^2-y^2}$  and Onn- $p_x$ , Onn- $p_y$ , and Onn- $p_z$  character.

-Then the charge state of the impurity can modify the structural relaxations around the impurity and strongly affect the EFG.

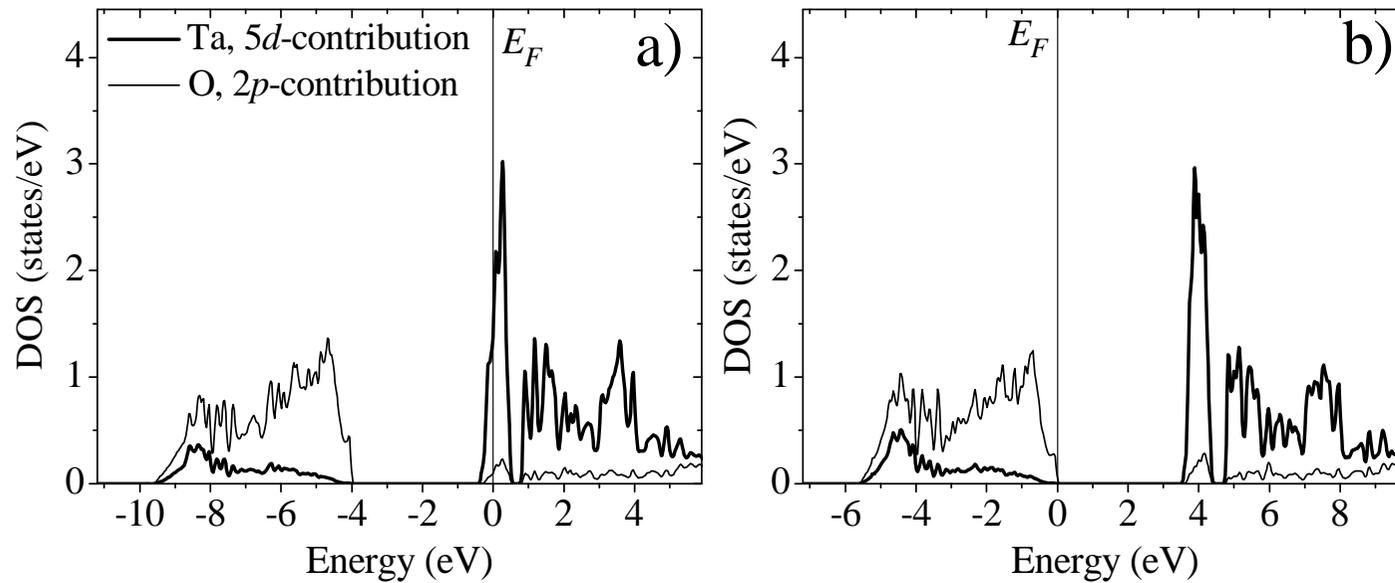
-The question that arises here is the charge state of the impurity that corresponds to the experimental results.



For this reason, calculations assuming two different physical situations were performed:

i- It was assumed a neutral Ta substitutes Hf in  $m\text{-HfO}_2$ . We will name this charge state “neutral charge state” ( $q = 0$ ). In this neutral charge state, the impurity state located at the Fermi level is partially occupied.

ii- In the real sample, the presence of defects (vacancies, interstitial atoms, the presence of donor or acceptors impurities) or thermal effects can change the charge state of the impurity. In order to investigate this point, we have performed calculations removing ( $q = +1$ ) one electron to the whole system ( $q = +1$ ). This impurity state is referred to as “charged state”.



- There is an almost “rigid band” behavior of the DOS, where the removal of one electron has the only effect of making the impurity level at the top of the valence band empty.

-The substitution of an Hf atom by a Ta impurity produces non-negligible forces on its nearest neighbors

-the amount of structural relaxation per atom decreases rapidly from the Onn to further shells.

-The EFG at the Ta site is essentially not affected by the relaxation of atoms lying beyond the Onn distance.

- The structural distortions strongly depend on the charge state of the impurity.

-For both charge states, a contraction of the Ta-Onn bonds was found.

		$q = 0$		$q = +1$	
$d(\text{Ta-Onn})$	Un-relaxed	LDA	GGA	LDA	GGA
$d(\text{Ta-O1})$	2.03	2.00	2.01	1.94	1.95
$d(\text{Ta-O2})$	2.07	2.01	2.02	1.96	1.99
$d(\text{Ta-O3})$	2.13	2.06	2.08	2.05	2.09
$d(\text{Ta-O4})$	2.14	2.11	2.10	2.07	2.09
$d(\text{Ta-O5})$	2.17	2.13	2.15	2.08	2.10
$d(\text{Ta-O6})$	2.23	2.22	2.21	2.28	2.25
$d(\text{Ta-O7})$	2.25	2.22	2.23	2.22	2.23

- The magnitude of the contractions is larger in the case of the charged impurity state.

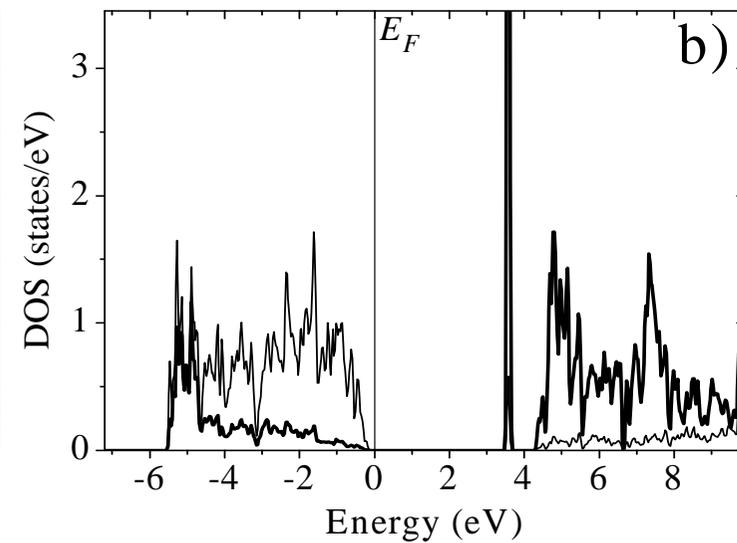
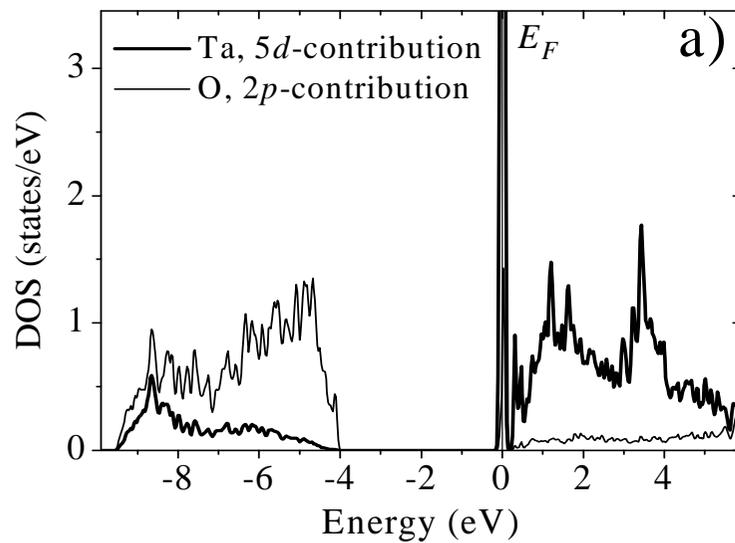
-The contractions of the Ta-Onn bond lengths can be understood from the fact that the bond lengths in tantalum oxide ( $\text{TaO}_2$ ) are about 2.02 Å. It seems that the local structure tries to reconstruct the environment of Ta in its oxide

- The resulting EFGs obtained with the LDA and the GGA approximations are very similar.
- The difference in the EFGs obtained for the charged and the neutral cells is remarkable, and is not only caused by the different equilibrium structures obtained for each charge state. **We will return to this point**
- Finally, the obtained predictions are in poor agreement with the experimental results
- We will see that this discrepancy is related to the high Ta concentration compared to that used in the sample of in the experiment.

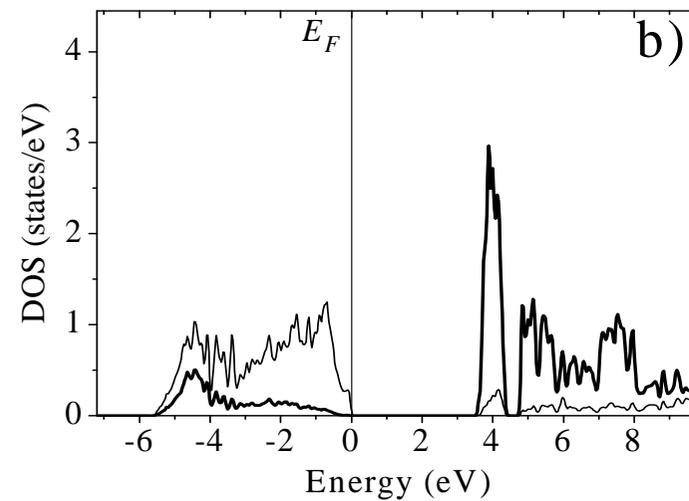
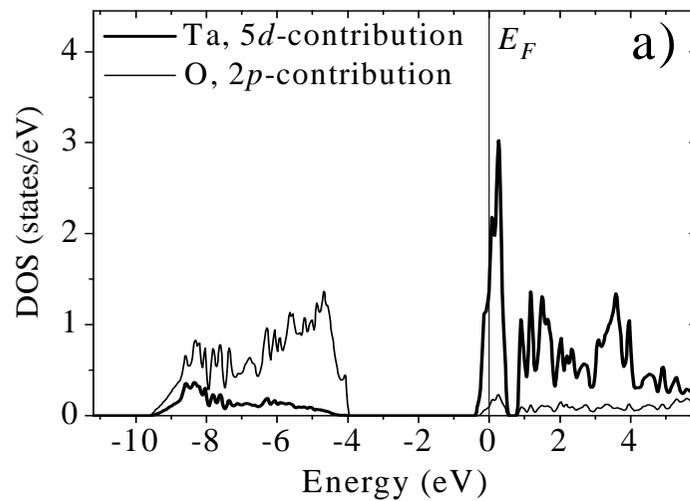
		q= 0		q = +1	
		LDA	GGA	LDA	GGA
<i>12 atoms-cell</i> <i>(Hf<sub>3</sub>TaO<sub>8</sub>)</i>	$V_{ZZ}$	+16.3	+16.9	+18.4	+18.7
	$\eta$	0.30	0.32	0.10	0.10



- The previous results presented for Ta in *m*-HfO<sub>2</sub> using a small cell had a Ta concentration that is by far **too high** to allow a meaningful comparison with TDPAC experiments.
- The interaction between **Ta neighbors cannot be neglected**, and the structural relaxation of the Ta nearest neighbors can be constrained by this **spurious interaction**.
- Therefore calculations using a much larger supercell were performed.
- Again both the LDA and GGA approximations were applied, but since the two approaches gave very similar results, only those obtained with GGA are included here.



- The Ta-*d* band is described as very sharp peaks indicating that interaction between Ta atoms is quite small for this supercell



- For the two charge states, reductions of the Ta-Onn bond lengths were found. - These results follow the tendency predicted in the previous calculation with the much smaller cell
- The structural distortion depends on the charge state of the impurity
- There are small differences between the equilibrium bond lengths predicted for the systems  $\text{Hf}_3\text{TaO}_8$  and  $\text{Hf}_{31}\text{TaO}_{64}$
- Structural distortion induced by the Ta impurity depends on the impurity concentration.
- As the EFG generally decays as  $1/r^3$ , where  $r$  is a measure of distance from the producing charge density, it is particularly sensitive to slight local changes. For this reason, these small differences in the position of the Ta neighbors (especially the oxygen first neighbors) **can strongly affect the EFG tensor.**

	Un-relaxed	$\text{Hf}_3\text{TaO}_{12}$		$\text{Hf}_{31}\text{TaO}_{64}$	
		$q = 0$	$q = +1$	$q = 0$	$q = +1$
$d(\text{Ta-Onn})$					
$d(\text{Ta-O1})$	2.03	2.00	1.95	2.01	1.97
$d(\text{Ta-O2})$	2.07	2.01	1.99	2.03	1.98
$d(\text{Ta-O3})$	2.13	2.06	2.09	2.10	2.06
$d(\text{Ta-O4})$	2.14	2.11	2.09	2.08	2.08
$d(\text{Ta-O5})$	2.17	2.13	2.10	2.14	2.08
$d(\text{Ta-O6})$	2.23	2.22	2.25	2.17	2.15
$d(\text{Ta-O7})$	2.25	2.22	2.23	2.21	2.18

		q= 0		q = +1		Experimental results
		LDA	GGA	LDA	GGA	
12 atoms-cell (Hf <sub>3</sub> TaO <sub>8</sub> )	V <sub>ZZ</sub>	+16.3	+16.9	+18.4	+18.7	1 <sup>st</sup> QI: V <sub>ZZ</sub> = 13.7 <sub>1</sub> η = 0.340 <sub>3</sub>
	η	0.30	0.32	0.10	0.10	
96 atoms-cell (Hf <sub>31</sub> TaO <sub>64</sub> )	V <sub>ZZ</sub>	-	+21.2	-	+13.6	2 <sup>nd</sup> QI V <sub>ZZ</sub> = 22.5+-1.8 η = 0.3-0.4
	η	-	0.29	-	0.40	

-There is a clear increase in the magnitude of  $V_{ZZ}$  going from the 12-atom cell to the 96-atom supercell, and the asymmetry parameter changes from 0.32 to 0.29. In the case of the charged cell, the magnitude of  $V_{ZZ}$  decreases from  $18.7 \times 10^{21}$  V/m<sup>2</sup> to  $+13.6 \times 10^{21}$  V/m<sup>2</sup> going from the 12-atoms cell to the 96-atoms supercell.

- The agreement between the calculated and the experimental is excellent, for both QI detected for the Ta TDPAC probes.

-Tests performed with large SC do not introduce modifications on the results, enabling us to conclude that the Ta dilution is converged.

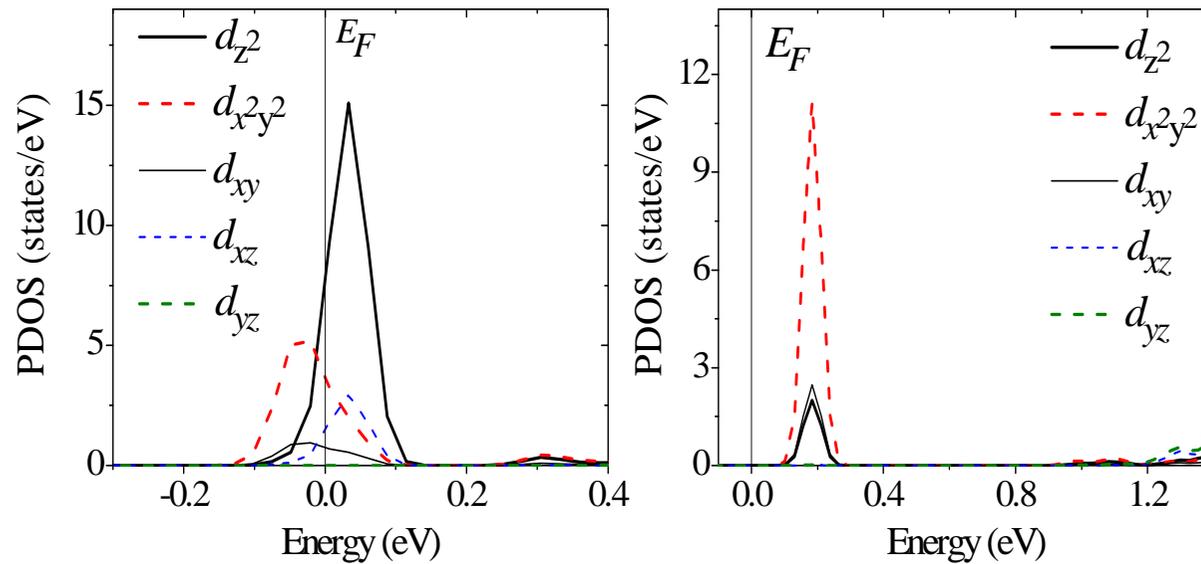
- As discussed earlier, the EFG strongly depends on the Ta concentration. Since different concentrations produce different structural distortions, it is interesting to separate the **electronic** and **structural** effects.
- In order to do that, we have taken the 12-atom cell and we fixed the Ta atom and its O<sub>nn</sub> at the equilibrium positions predicted for the system Hf<sub>31</sub>TaO<sub>64</sub>.
- At this position we calculated the EFG tensor at the Ta site. We obtain for the neutral cell ( $q = 0$ )  $V_{ZZ} = +11.5 \times 10^{21}$  V/m<sup>2</sup> and  $\eta = 0.47$ .
- Besides the fact that the symmetry is similar to those found for the system Hf<sub>31</sub>TaO<sub>64</sub> ( $\eta = 0.40$ ), the magnitude of  $V_{ZZ}$  is very different to those predicted for the large unit cell ( $V_{ZZ} = +21.2 \times 10^{21}$  V/m<sup>2</sup> )
- This calculation shows that there is a **large Ta-Ta** interaction in the case of the smaller cell that affects the structural relaxations and also the EFG when equal positions for the ions are considered. Similar conclusions were drawn in the case of the charged system.

-In order to investigate the origin of the difference in the EFG for the two charge-states of the impurity we concentrate in the valence contribution to the EFG which originates in the asymmetry of the valence charge distribution inside the muffin-tin sphere .

-In all cases, the so-called “valence” EFG dominates, while the “semicore” as well as the “lattice” term are almost negligible. The dominant valence contribution can be split in the different orbital symmetries.

- The largest differences are found for the  $d$  contributions to  $V_{ZZ}$ . These  $d$  differences originate in the filling of the impurity state at the Fermi level that has important  $Ta-d_z^2$  and  $Ta-d_{x^2-y^2}^2$  contributions, as can be seen in Figs.6 a. and 6.b.

	$q - 0$			$q - +1$		
	$V_{ZZ}$	$V_{YY}$	$V_{XX}$	$V_{ZZ}$	$V_{YY}$	$V_{XX}$
$p$	+8.9	-7.1	-1.8	+12.8	-8.8	-4.0
$d$	+15.3	-10.2	-5.1	+1.0	-1.0	0.0
$s-d$	+0.22	-0.18	-0.04	+0.22	-0.12	-0.10
Total-valence	+24.5	-17.4	-7.06	+14.1	-10.0	-4.1



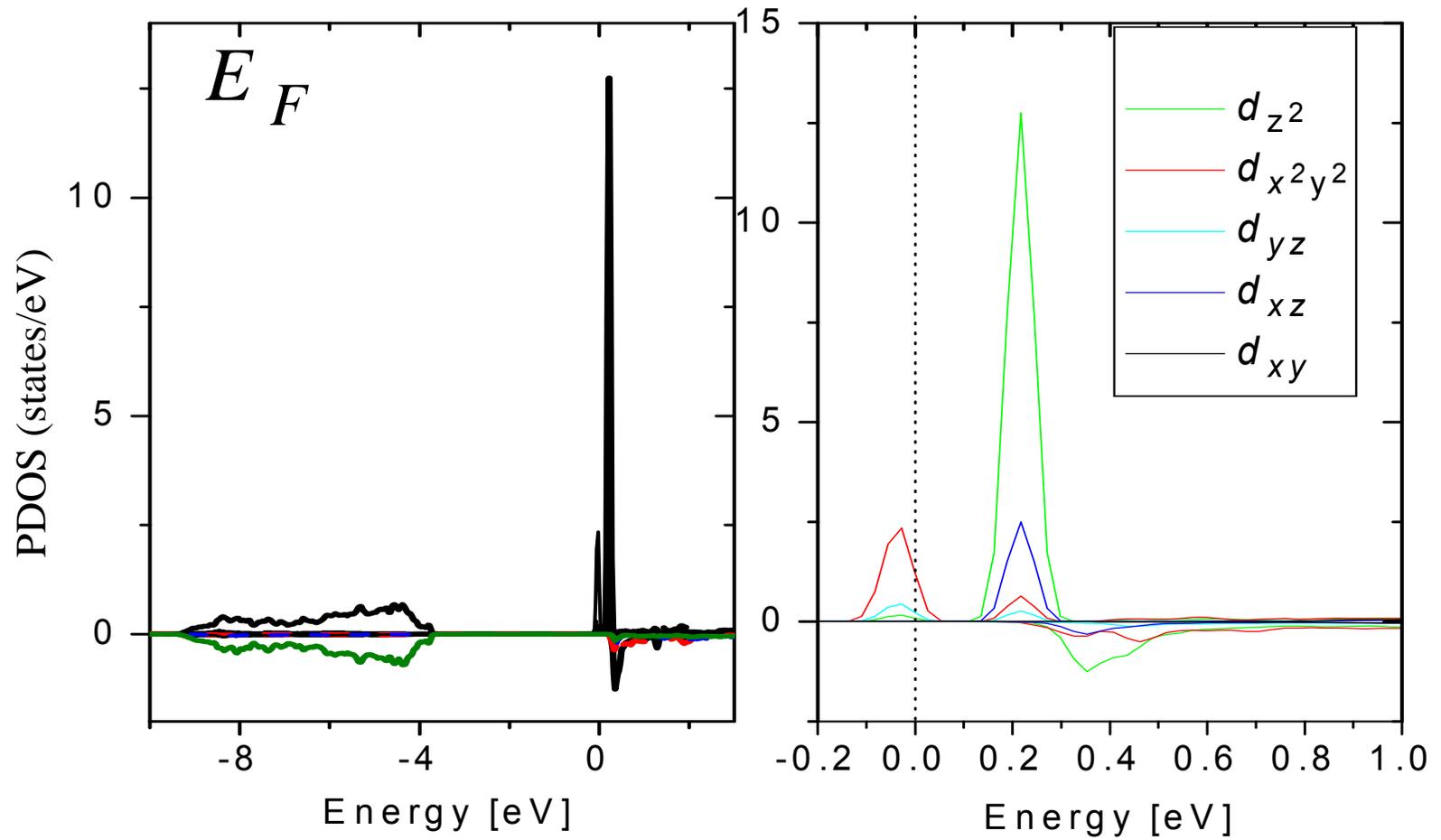
Atom-resolved PDOS for Ta atom in the relaxed 96 atoms-supercell for a) the neutral charge state ( $q = 0$ ) and b) the charged state ( $q = +1$ ) of the impurity.

## But what about Magnetism?

- Charged state ( $q = +1$ ,  $V_{ZZ} = 13.7_1$ ,  $\eta = 0.340_3$ ) has an even number of electrons.
  - Neutral state ( $q = 0$ ,  $V_{ZZ} = 22.5 \pm 1.8$ ,  $\eta = 0.3-0.4$ ) has an odd number of electrons.
- So, now that everything related with convergence of the Ta dilution is resolved, is time to see what happens with spin polarized calculations

-For  $q=+1$  nothing changes

- For  $q=0$ :





-Considering Total Energy:

-2x2x2 cell  $\Delta E=0.004$  Ry favorable to magnetic calculation (**which is near to the order of magnitude of the convergence error**)

-2x2x4 cell  $\Delta E=0.01$  Ry favorable to magnetic calculation (out of convergence errors)

-Spin Magnetic Moment in cell  $\sim 1\mu_B$



-At present, there is no experimental evidence of a magnetic phase in Ta-doped HfO<sub>2</sub>.

-In the presence of a magnetic phase, the hyperfine interaction should be mixed **cuadрупolar electric** (QI) and **bipolar magnetic**.

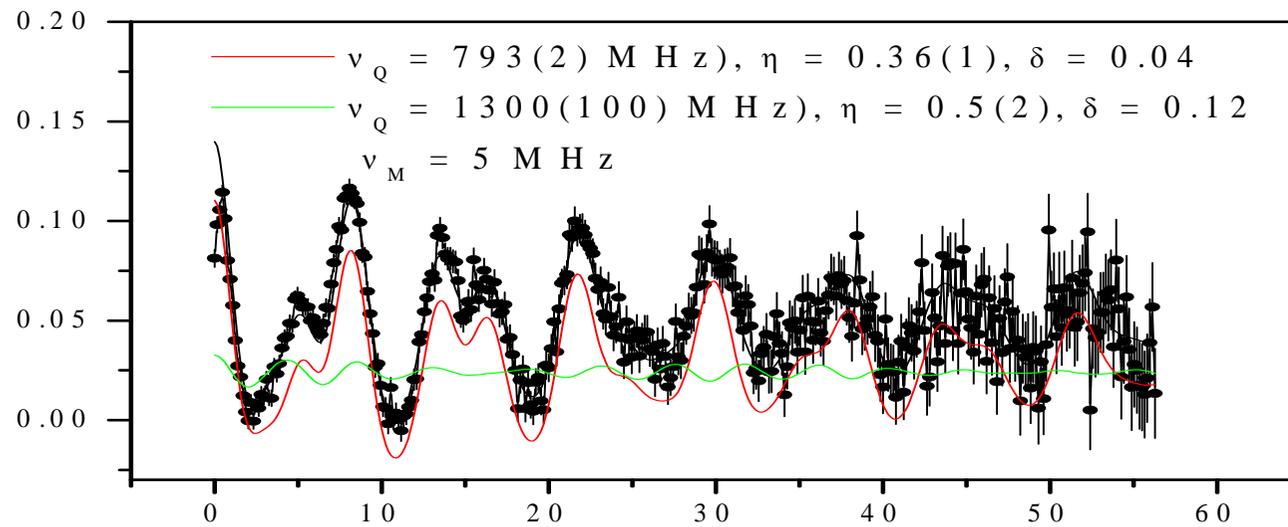
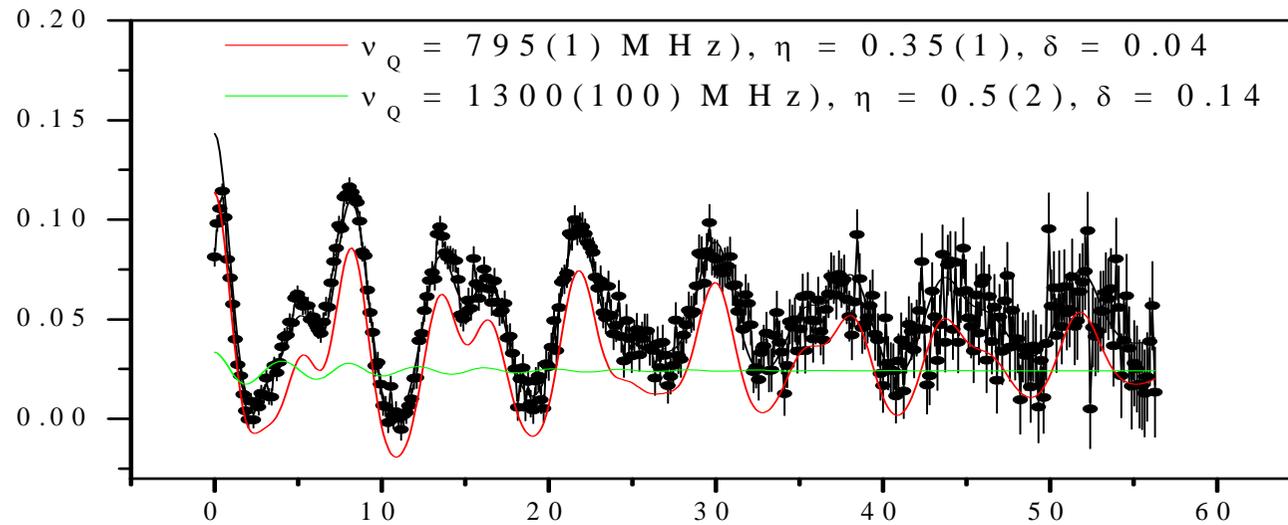
-In the recent TDPAC experiments there is nothing reported related to magnetism.

-Should the experimenters detect this magnetic ordering?

- $\mu(\text{Ta})$  is too low so, in the presence of a strong QI, the magnetic interaction can not be distinguished.

-Further experiments with other techniques should be necessary.

T 300 K , after 1400 K



Time (ns)

## Conclusions

- DFT (and APW+LO inside) lead to accurate predictions on EFG in  $\text{HfO}_2$
- Both QI experimentally detected are explained
- Analysis of the charge state of impurities becomes highly relevant
- For the first time it is given a different interpretation of the low populated QI at the Ta probes which is not related with defects or surface (grain boundaries) effects.
- We obtain another example of the complexity of the analysis of probe-needed hyperfine spectroscopies related with the introduction of the impurity, which can not be approached by simple models.
- The presence of the impurity can lead the material to a ferromagnetic state

- Also, this magnetism in bulk is not related with other effect than the presence of the impurity.
- TDPAC experiments would not be able to resolve this magnetic interaction.
- New experiments needed.

## Open questions

- What is the mechanism that allow the coexistence of two different charge states in a real sample?
- What can be done (addition of impurities, vacancies, surfaces?) to allow the full impurity state to go below  $E_f$  in order to augment the magnetic moment.