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Nature of the $\mathrm{Fe}_{\frac{4}{2}}$ center in $\mathrm{KTaO_3}$: A density functional theory study

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This work is aimed at clearing out the nature of the axial $\mathrm{Fe}_{\frac{4}{2}}$ center detected by electron-paramagnetic resonance in iron-doped $\mathrm{KTaO_3}$ for which two different models have been put forward. While some authors ascribe such a center to a Fe^+ impurity at a K^+ site, although suffering an off-center motion along $\langle 001\rangle$ directions, other groups propose that the $\mathrm{Fe}_{\frac{4}{2}}$ center involves a Fe^{5+} ion at a Ta^{5+} site, which later also undergoes an off-center shift along a principal direction of the $\mathrm{KTaO_3}$ lattice. Seeking to clarify this puzzling situation, the possible off-center shift of both Fe^{5+} and Fe^+ impurities in $\mathrm{KTaO_3}$ is explored in this work by means of density functional calculations. As a salient feature it is shown that there is a huge barrier that prevents the motion of Fe^{5+} against one of the closest O^{2-} anions. The case of Fe^+ at a K^+ site is more complex as the energy difference (10Dq) between the lower-lying e_g ($\sim x^2$-y^2,$3z^2$-r^2) and t_{2g} ($\sim xy,xz,yz$) O_h levels is found to be equal to only -0.038 eV, and thus several states as a function of the displacement coordinate Z_{Fe} have to be explored in order to determine what is the actual ground state and the associated equilibrium coordinate Z^0_{Fe}. The ground state is found to correspond to the $b_1(x^2$-$y^2)^1$ $a_1(3z^2$-$r^2)^2$ $b_2(xy)^2$ $e(xz,yz)^2$ C_{4v} configuration with spin $S=3/2$ and $Z^0_{\mathrm{Fe}}=90$ pm, thus involving a significant off-center motion from the K^+ site, which is found to be accompanied by a small ligand relaxation. As a salient feature this ground state is different from that derived constraining Fe^+ at the K^+ site. The present calculations also reproduce the experimental feature $g_\perp - g_0 > g_\parallel - g_0$ observed for the $\mathrm{Fe}_{\frac{4}{2}}$ center. An analysis of first-excited states at equilibrium allows one to understand this fingerprint in a simple way.

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I. INTRODUCTION

A great deal of research is currently focused on transition-metal oxides as they exhibit a huge variety of unusual and interesting physical phenomena going from the colossal magnetoresistance to ferroelectricity.[1–5] In the domain of ferroelectrics, particular attention is paid to the influence of impurities on the ferroelectric transition.[6] This is especially true in the case of the so-called incipient ferroelectrics such as $\mathrm{SrTiO_3}$ and $\mathrm{KTaO_3}$.[6–24] Although these compounds have a polar soft mode, the ferroelectric phase transition down to $T=0$ K is suppressed by quantum fluctuations associated with the zero-point energy.[25–27] For this reason the formation of defect-induced polar states in incipient ferroelectrics has attracted considerable attention in recent years.[19–24]

An important role on the properties of $\mathrm{SrTiO_3}$ and $\mathrm{KTaO_3}$ is played by $3d$ impurities, which often display an open-shell electronic structure. For this reason a tool such as electron-paramagnetic resonance (EPR) is suitable for exploring the nature, location, and local geometry of a given $3d$ impurity in these materials.[6–10,12–16,18–22,24] However, the power of the EPR technique is reduced in the case of oxides due to two main reasons.[12,14,22] On one hand, as 99.97% of natural oxygen is made of the $^{16}\mathrm{O}$ isotope, which has zero nuclear spin, the hyperfine interaction with ligands (called superhyperfine) is suppressed. This is thus contrary to what happens in halides host lattices where the detection of the superhyperfine structure provides key information on the nature and number of ligands and even, in some cases, on the value of impurity-ligand distances. On the other hand, sometimes the center associated with a transition-metal impurity is complex as it involves a vacancy, another impurity, or merely the impurity shift from a lattice site with high symmetry. If the ground state of the impurity has a spin $S>1/2$ this leads to the appearance of the zero-field splitting term in the spin Hamiltonian. For an axial symmetry this term is written as (Ref. 28) $H_{\mathrm{ZFS}}=D[S_Z^2-S(S+1)/3]$. When D becomes much more important than the Zeeman term and S is half integer this avoids the observation of all the allowed transitions in the ground-state manifold with the exception of the $-1/2 \rightarrow 1/2$ transition, which does not depend on the D value. In such a situation the available EPR information is described by an effective spin $S_{\mathrm{eff}}=1/2$ and, thus, it is not easy (in principle) to know the actual value of S corresponding to the ground state of the impurity. It is worth noting however that the effective $g_\perp^{\mathrm{eff}}$ and $g_\parallel^{\mathrm{eff}}$ values (derived under the assumption that the actual spin is S_{eff}) are related to S and the true $g_\perp$ and $g_\parallel$ values by[28]

$$g_\parallel^{\mathrm{eff}} = g_\parallel, \quad g_\perp^{\mathrm{eff}} = (S+1/2)g_\perp. \tag{1}$$

Due to the usual quenching of the orbital angular momentum for transition-metal impurities some information on S can thus be gained from the $g_\perp^{\mathrm{eff}}$ experimental value.

A relevant example showing the limitations of the EPR technique for properly identifying the nature and location of impurities in oxides is provided by the so-called axial $\mathrm{Fe}_{\frac{4}{2}}$ center formed in $\mathrm{KTaO_3}$ even in unintentionally doped samples.[10,12,14–16,18,22] This center is described by $S_{\mathrm{eff}}=\frac{1}{2}$, $g_\perp^{\mathrm{eff}}=4.33$, and $g_\parallel^{\mathrm{eff}}=2.02$ (center name coming from

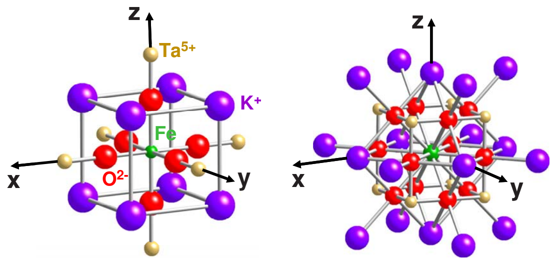

FIG. 1. (Color online) Left: 21-atom cluster used in the calculations of the Fe_{Ta}^{5+} center in $KTaO_3$. Right: 39-atom cluster used for the Fe_K^+ center.

$g_{\parallel}^{\mathrm{eff}}/g_{\parallel}^{\mathrm{eff}} \approx 4/2$) and the principal direction associated with $g_{\parallel}^{\mathrm{eff}}$ is a ⟨001⟩-type direction of the host lattice. The $Fe_{\frac{4}{2}}$ center was first observed by EPR by Abraham *et al.*[10] and attributed to a Fe^{3+} impurity. Later, Glinchuk *et al.*[12,14] pointed out that, according to Eq. (1) and the experimental value $g_{\perp}^{\mathrm{eff}}=4.33$, the iron impurity present in the $Fe_{\frac{4}{2}}$ center can hardly be associated with $S=5/2$ and thus with a nominal charge of +3. By contrast, it was remarked that the experimental value $g_{\perp}^{\mathrm{eff}}=4.33$ fits better with $S=3/2$. According to this view both Fe^{5+} ($3d^3$) and Fe^+ ($3d^7$) ions could be involved in the $Fe_{\frac{4}{2}}$ center. Furthermore, assuming that $S=3/2$ the experimental $g_{\perp}^{\mathrm{eff}}=4.33$ and $g_{\parallel}^{\mathrm{eff}}=2.02$ values lead to $g_{\parallel}=2.02$ and $g_{\perp}=2.16$ using Eq. (1). As both $g_{\parallel}$ and $g_{\perp}$ are *higher than* the gyromagnetic ratio of a free electron ($g_0=2.0023$), this fact suggests that the number of electrons involved in the Fe^{q+} impurity would be higher than 5 in order to have a hole configuration. In view of this reasoning, Glinchuk *et al.*[12,14] proposed that Fe^+ is actually behind the $Fe_{\frac{4}{2}}$ center found in $KTaO_3$. As pointed out above, EPR spectra described by $S_{\mathrm{eff}}=\frac{1}{2}$ and $g_{\perp}^{\mathrm{eff}}=4.33$ strongly suggest the existence of a huge zero-field splitting. For this reason Glinchuk *et al.*[12,14] put forward that Fe^+ is not lying at a K^+ site with a dodecahedral coordination but undergoes an off-center shift from that position along ⟨001⟩ directions. This assignment for the $Fe_{\frac{4}{2}}$ center will be shortly referred to as Fe_K^+. A pictorial description of the Fe_K^+ center is given in Fig. 1.

It is worthwhile to remark here that a rather different description of the $Fe_{\frac{4}{2}}$ center has been proposed by other authors. Although hyperfine interactions with ^{16}O nuclei are rigorously excluded, Bursian *et al.*[18] detected the hyperfine interaction with ^{181}Ta nuclei. These authors noticed that the ^{181}Ta hyperfine constants observed for the $Fe_{\frac{4}{2}}$ center are similar to those previously measured for the cubic Fe^{3+} center formed in $KTaO_3$, where the Fe^{3+} impurity is located at the Ta^{5+} site. On this basis, Bursian *et al.*[18] proposed that the $Fe_{\frac{4}{2}}$ center actually comes from a Fe^{5+} ion although it is not located at the Ta^{5+} site. In this sense these authors suggest that the strong anisotropy of the center could be caused by an off-center displacement of the Fe^{5+} ion along ⟨001⟩ directions. Furthermore, they propose that the off-center motion would arise from the smaller ionic radius of Fe^{5+} (estimated in the 40–50 pm range) when compared to that of Ta^{5+} (64 pm). Hence, this model for the $Fe_{\frac{4}{2}}$ center will be referred to as Fe_{Ta}^{5+}. A pictorial description of Fe_K^+ center is also given in Fig. 1. It should be stressed that this description of the $Fe_{\frac{4}{2}}$ center is also shared by Baranov *et al.*,[22] who recently performed EPR measurements on the $Fe_{\frac{4}{2}}$ center in ^{57}Fe-doped $KTaO_3$ demonstrating unambiguously that iron is involved in that center.

Ab initio calculations can certainly be of help for clarifying this somewhat puzzling situation.[29] This work is aimed at exploring the actual nature of the $Fe_{\frac{4}{2}}$ center formed in $KTaO_3$ by means of density functional theory (DFT)-based calculations. In order to achieve this goal the possible off-center displacement for both Fe^{5+} and Fe^+ impurities in $KTaO_3$ is investigated in detail. In this research particular attention is paid to determine what are the actual ground state and the associated value of the spin. This investigation is especially troublesome in the case of the Fe_K^+ center because the separation between e_g and t_{2g} electrons in a dodecahedral coordination is found to be only of the order of 5×10^{-2} eV. Bearing in mind the smallness of this figure and that an additional splitting of these levels is caused by an off-center displacement from the K^+ site, several electronic configurations have to be checked in order to determine which of them corresponds to the electronic ground state.

This article is arranged as follows: Relevant computational details are provided in Sec. II, while in Sec. III the main results obtained in this work are reported. Apart from exploring the possible off-center shift for both Fe_{Ta}^{5+} and Fe_K^+ models of the $Fe_{\frac{4}{2}}$ center, attention is paid to understand the main features of the experimental g tensor of this center. Finally, some remarks are added in the Sec. IV.

II. COMPUTATIONAL DETAILS

DFT calculations have been carried out by means of the Amsterdam density functional (ADF) code[30] using various exchange-correlation functionals: the Vosko-Wilk-Nusair[31] one in the local-density approximation (LDA) and the generalized gradient approximation (GGA) in its Becke-Perdew (BP) (Refs. 32 and 33) and Becke-Lee-Yang-Parr[32,34] forms. The employed basis sets are consisted of three Slater-type orbitals plus a polarization function per atomic orbital as implemented in the ADF program. We used the basis that contained the larger frozen core available in the database as these orbitals play only a minor role in the studied properties.

Calculations for Fe_K^+ and Fe_{Ta}^{5+} centers in $KTaO_3$ have been carried out using the cluster approximation. Previous results[29,35,36] obtained for Ni^+-, Cu^{2+}-, and Fe^+-doped MF_2 ($M=Ca,Sr$) and $SrCl_2$ showed that the off-center motion is well reproduced by small size clusters containing only 21 atoms because the active $3d$ electrons are localized to a good extent in the region formed by the impurity and ligands. In the present work, clusters of 21 ($FeO_6K_8Ta_6^{27+}$) and 39 ($FeO_{12}Ta_8K_{18}^{47+}$) ions centered at the Fe impurity (Fig. 1) have been used to simulate, respectively, the Fe_{Ta}^{5+} and Fe_K^+ centers in $KTaO_3$. In order to show the reliability of calculations performed on these clusters, some results obtained for clusters of different sizes will be presented. In the geometry optimizations performed on all these clusters, only the atomic positions of Fe ion and O ligands have been allowed to vary, the rest of ions are fixed at the experimental host-lattice positions. Calculations have been performed for clusters *in vacuo* as the electrostatic potential due to the rest of

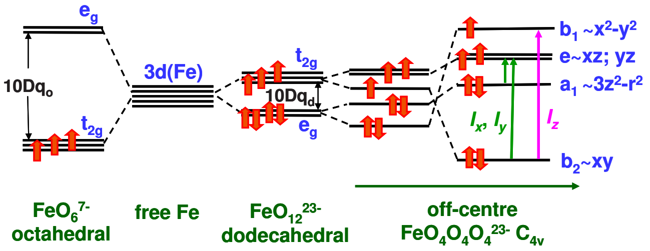

FIG. 2. (Color online) Qualitative scheme depicting the splitting of the main 3d(Fe) one-electron levels for octahedral FeO$_6^{7-}$ (left) and dodecahedral FeO$_{12}^{23-}$ (right) complexes. In the last complex, the shift of the levels under an increasing Z_{Fe} off-center distortion of the Fe$^+$ cation, producing a FeO$_4$O$_4$O$_4^{23-}$ C_{4v} complex, is also indicated.

the lattice on the cluster region is found to be very flat in cubic oxoperovskites.

In order to check the LDA and GGA results, some calculations were also carried out using the three parameter hybrid semiempirical B3LYP functional[37] implemented in the GAUSSIAN 98 package.[38] These calculations use the double zeta LANL2DZ basis, which contains Gaussian-type orbitals and pseudopotentials to simulate the core electrons. The obtained results are similar to the corresponding LDA and GGA values.

Most of the calculations have been performed using the spin-restricted approach but we have checked that results are very similar using spin-unrestricted calculations. Spin-unrestricted calculations including spin-orbit corrections of the g tensor in both centers have also carried out using the EPR module of the ADF code.[29]

III. RESULTS AND DISCUSSION

A. Equilibrium geometry of the Fe$^{5+}_{\mathrm{Ta}}$ center

One of the proposed models for the Fe$_2^4$ center in KTaO$_3$ involves a Fe^{5+} ion (3d^3 electronic configuration) at a Ta^{5+} site, which later undergoes an off-center displacement of the Fe^{5+} ion along ⟨001⟩ directions (Fig. 1). For this reason, in a first step the value of the Fe-O distance R_{ML}, keeping Fe^{5+} ion at the Ta^{5+} site, has been calculated for the electronic ground state. As Fe^{5+} is isoelectronic with the well-known Cr^{3+} impurity in oxides,[39,40] the ground state of the octahedral FeO$_6^{7-}$ complex is $^3A_{1g}(t_{2g}^3)$ as shown in Fig. 2.

Looking for the equilibrium geometry of the Fe$^{5+}_{\mathrm{Ta}}$ center in KTaO$_3$, optimizations on the 21-ion FeO$_6$K$_8$Ta$_6^{27+}$ cluster at the $^3A_{1g}$ ground state have been carried out using the four exchange-correlation functionals previously indicated. We have verified that the calculated R_{ML} values are all coincident within 1%. Moreover, some optimizations have also been performed on the 27-ion FeO$_6$K$_8$Ta$_6$O$_6^{15+}$ cluster. Using the GGA-BP functional, the calculated equilibrium value of the Fe-O distance R_{ML} was found to be equal to 206.3 and 207.0 pm for the 21- and 27-ion clusters, respectively. It is worth noting that these values are a bit higher than the experimental Ta-O distance in the host lattice equal to $a/2=199.4$ pm (a is the cubic lattice parameter).[41] This ∼3.5% outward relaxation produced under the Ta^{5+}→Fe^{5+} substitution thus stresses that the size of Fe^{5+} is certainly not significantly smaller than that of Ta^{5+}. This fact is partially related to covalent effects present in every transition-metal complex with closed-shell ligands, leading to a net transfer of electronic charge from them to the central cation. In the present case the Mulliken charge on iron for the Fe$^{5+}_{\mathrm{Ta}}$ center is found to be equal to $+1.1e$ (e denotes the proton charge), which is substantially smaller than the nominal value of $+5e$. Interestingly, the value at equilibrium of the energy separation between e_g ($\sim x^2-y^2$, $3z^2-r^2$) and t_{2g} ($\sim xy,xz,yz$) levels of the O$_h$ FeO$_6^{7-}$ complex, 10Dq, is calculated to be equal to 1.0 eV. This figure is much bigger than the corresponding value computed for Fe$^+$ in dodecahedral coordination—a matter discussed in Sec. III B.

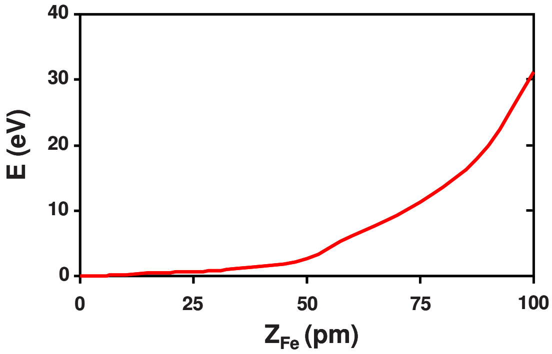

FIG. 3. (Color online) Profiles of the DFT total energy of the Fe$^{5+}_{\mathrm{Ta}}$ center as a function of the Z_{Fe} coordinate calculated for the $xy^1xz^1yz^1$ electronic configuration. Results correspond to GGA-BP calculations for the 21-atom cluster.

In a second step the hypothetical off-center displacement of the Fe^{5+} ion along ⟨001⟩ directions has been explored through DFT calculations. The total energy E of the C_{4v} FeO$_6$K$_8$Ta$_6^{27+}$ cluster has been calculated as a function of the Z_{Fe} coordinate, related to the displacement of the impurity along a ⟨001⟩ direction, keeping the rest of cluster ions at their equilibrium positions. Bearing in mind the calculated value 10 Dq≈1.0 eV for $Z_{\mathrm{Fe}}=0$, the ground state has been considered to be described by $xy^1xz^1yz^1$ coming from the t_{2g}^3 configuration in O$_h$ symmetry. As shown in Fig. 3, the $E(Z_{\mathrm{Fe}})$ profile obtained for this ground state has a single minimum at $Z_{\mathrm{Fe}}=0$ and exhibits a huge barrier, which precludes the existence of any off-center displacement along ⟨001⟩ directions. Specifically, such a barrier is equal to 2 eV when $Z_{\mathrm{Fe}}=40$ pm while it reaches a 30 eV value when Z_{Fe} is equal to 100 pm. We have verified that this big barrier comes from the overlapping of electronic clouds of the impurity and the closest ligand (placed at a distance equal to R_{ML}-Z_{Fe}), which increases substantially when Z_{Fe} does. This phenomenon is described, in a phenomenological way, by the Born-Mayer repulsion term and acts against the decrease in electrostatic energy obtained considering all ions as point charges. Specifically, this electrostatic energy gain is found to be equal only to 0.1 and 4 eV for $Z_{\mathrm{Fe}}=40$ and 100 pm, respectively. By virtue of this fact, it is hard to imagine that a significant off-center displacement in a perovskite or a NaCl-type lattice involves the motion of the impurity *against* one of the *closest* anions. Along this line experimental data on systems such as KCl:Li$^+$ (Ref. 42) or KBr:Cu$^+$ (Ref. 43) indicate that the impurity undergoes an off-center shift although the displacement does not happen along a $\langle 001 \rangle$ direction but along $\langle 111 \rangle$. For this reason, additional calculations were also carried out to check the possibility of an off-center displacement of the Fe^{5+} ion along the $\langle 111 \rangle$ axis. The results of these calculations also indicate that, in the present case, a spontaneous movement in this direction is again not allowed.

For the sake of completeness we have also verified that the $E(Z_{\mathrm{Fe}})$ curves corresponding to the first-excited configurations with $S=3/2$ are placed too high in energy to cross the curve corresponding to the ground state.

In conclusion, the present calculations support that if the Fe_2^4 center involves a Fe^{5+} ion at the Ta^{5+} site, the impurity is not allowed to do any off-center excursion. This situation is thus similar to that found for the isoelectronic Cr^{3+} impurity in oxides.[37,38] Therefore, as the EPR signal of the Fe_2^4 center exhibits a clear tetragonal angular pattern[10,12,14–16,18,22] iron can hardly be present as Fe^{5+} in such a center.

B. Geometry optimizations for $\mathrm{Fe}_{\mathrm{K}}^{+}$ center

Let us now explore by means of DFT calculations the model for the Fe_2^4 center put forward by Glinchuk *et al.*[12,14] (Fig. 1). In this model iron is present as a Fe$^+$ ($3d^7$) impurity, replacing the monovalent K$^+$ ion of the KTaO$_3$ lattice, although it undergoes a spontaneous off-center shift along a $\langle 001 \rangle$ direction. It should be noted that, in this case, the direction of this motion *does not* correspond to any of the 12 directions joining the impurity with oxygen ligands under O$_h$ symmetry.

Similar to the study carried out for a Fe^{5+} ion, let us first have a look at results obtained constraining the Fe$^+$ ($3d^7$) impurity at the K$^+$ site where oxygen ligands display a dodecahedral coordination. It is worth noting that, contrary to what happens in octahedral coordination, t_{2g} levels are lying *above* e_g ones (implying that $10\mathrm{Dq}<0$) on moving to a hexahedral or dodecahedral coordination such as those shown in Fig. 2. Bearing in mind this fact and Hund's rules, the equilibrium Fe$^+$-O^{2-} distance R_{ML} has been derived for a ground-state $S=3/2$ and a $e_g^4 t_{2g}^3$ configuration. The calculated value $R_{\mathrm{ML}}=278.3$ pm is only a bit smaller than the experimental K$^+$-O^{2-} distance (282 pm) in the host lattice.[41] As expected, covalence effects are much smaller for a Fe$^+$ ($3d^7$) impurity than for Fe^{5+}. Along this line the Mulliken charge on iron for a FeO_{12}^{23-} complex is found to be equal to $0.7e$, which is not far from the nominal charge of the Fe$^+$ impurity.

The absolute value of 10Dq for a nominally monovalent impurity and in dodecahedral coordination is expected to be smaller than that for Fe^{5+} in octahedral coordination. The calculated value $10\mathrm{Dq}=-0.038$ eV is consistent with this view. At the same time this figure underlines that e_g and t_{2g} levels of FeO_{12}^{23-} are practically degenerate at the equilibrium distance. By virtue of this fact it is not easy to know *a priori* on what is the actual ground state corresponding to a given value of the off-center coordinate Z_{Fe}.

Let us now explore whether a Fe$^+$ impurity at a K$^+$ site can spontaneously move off center along a $\langle 001 \rangle$ direction. Bearing in mind the experimental results and the low 10Dq value in a perfect dodecahedral coordination, it is necessary to look into the seven possible electronic configurations with $S=3/2$.

TABLE I. Parameters obtained by means of DFT-BP calculations performed on the 39-atom cluster simulating the $\mathrm{Fe}_{\mathrm{K}}^{+}$ site KTaO$_3$ for seven C_{4v} electronic configurations with spin $S=3/2$. Configurations with three electrons at the $e(xz,yz)$ orbital have been calculated using C_{2v} symmetry in order to have one unpaired electron. E_C is the vertical excitation energy from the ground state at the reference geometry ($Z_{\mathrm{Fe}}=0$) and ΔE_0 is the energy of the minimum of each state with respect to the energy of the lowest state at $Z_{\mathrm{Fe}}=0$. Z_{Fe}^0 (given in pm) indicates the displacement of the Fe$^+$ ion at the minimum of energy of each configuration.

C_{4v} configuration	E_C	ΔE_0	Z_{Fe}^0
$b_1(x^2\text{-}y^2)^2 a_1(3z^2\text{-}r^2)^2 b_2(xy)^1 e(xz,yz)^2$	0	−0.03	20
$b_1(x^2\text{-}y^2)^1 a_1(3z^2\text{-}r^2)^2 b_2(xy)^2 e(xz,yz)^2$	0.06	−0.71	93
$b_1(x^2\text{-}y^2)^2 a_1(3z^2\text{-}r^2)^1 b_2(xy)^1 e(xz,yz)^3$	0.06	+0.06	0
$b_1(x^2\text{-}y^2)^1 a_1(3z^2\text{-}r^2)^1 b_2(xy)^2 e(xz,yz)^3$	0.26	−0.31	103
$b_1(x^2\text{-}y^2)^1 a_1(3z^2\text{-}r^2)^1 b_2(xy)^1 e(xz,yz)^4$	0.28	+0.28	0
$b_1(x^2\text{-}y^2)^1 a_1(3z^2\text{-}r^2)^2 b_2(xy)^1 e(xz,yz)^3$	0.69	+0.39	51
$b_1(x^2\text{-}y^2)^2 a_1(3z^2\text{-}r^2)^1 b_2(xy)^2 e(xz,yz)^2$	0.70	+0.61	63

Under a [001] displacement of the Fe$^+$ cation, t_{2g} and e_g levels of the O$_h$ FeO_{12}^{23-} complex split, respectively, in $b_2(\sim xy)$, $e(\sim xz,yz)$ and $b_1(\sim x^2-y^2)$, $a_1(\sim 3z^2-r^2)$ levels of the distorted C_{4v} $\mathrm{FeO}_4\mathrm{O}_4\mathrm{O}_4^{23-}$ complex (Fig. 2), which has three inequivalent groups of ligands. Total-energy calculations have been carried out on the 39-atom $\mathrm{FeO}_{12}\mathrm{Ta}_8\mathrm{K}_{18}^{47+}$ cluster (Fig. 1) for all possible configurations with $S=3/2$ corresponding to different occupations of mainly $3d$(Fe) levels with seven electrons. In the on-center geometry ($Z_{\mathrm{Fe}}=0$) the minimum-energy configuration is $b_1(x^2-y^2)^2$ $a_1(3z^2-r^2)^2$ $b_2(xy)^1$ $e(xz,yz)^2$ using the C_{4v} group notation. Taking the energy of this configuration as reference, the excitation energies E_C of the other six configurations with $S=3/2$ calculated at $R_{\mathrm{ML}}=278.3$ pm are shown in Table I. Configurations with three electrons at the $e(xz,yz)$ orbital have been calculated using C_{2v} symmetry in order to have one unpaired electron. Although these configurations are unstable (Jahn-Teller effect) we have verified that the corresponding distortions and stabilization energies are very small (~ 0.03 eV).

It can be noticed that the lowest-excited state with $S=3/2$ (corresponding to the $b_1^1 a_1^2 b_2^2 e^2$ configuration) lies only 0.06 eV above the ground state while the highest one (corresponding to the $b_1^2 a_1^1 b_2^2 e^2$ configuration) is placed at 0.70 eV. These facts can easily be rationalized through ligand field theory. In this framework, the energy of $b_1(x^2-y^2)^1$ $a_1(3z^2-r^2)^2$ $b_2(xy)^2$ $e(xz,yz)^2$ and $b_1(x^2-y^2)^2$ $a_1(3z^2-r^2)^1$ $b_2(xy)^2$ $e(xz,yz)^2$ states with respect to the ground state is just equal to $-10\mathrm{Dq}+B$ and $-10\mathrm{Dq}+9B$, respectively, where B is one of the two Racah parameters.

In a subsequent step we have investigated the influence of the off-center distortion on the energy of the seven electronic states, calculating the energy as a function of Z_{Fe}. As a first approximation the rest of ions are fixed at the positions previously determined when $Z_{\mathrm{Fe}}=0$. Particular attention has been paid to determine the value of Z_{Fe} at equilibrium Z_{Fe}^0 as

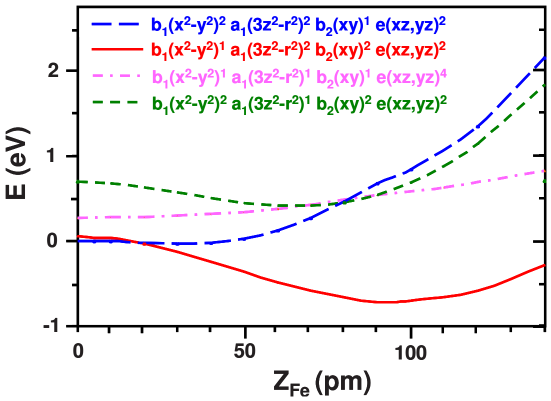

FIG. 4. (Color online) Profiles of the DFT total energy of the $\mathrm{Fe}_{\mathrm{K}}^{+}$ center as a function of the Z_{Fe} coordinate calculated for four $S=3/2$ electronic configurations. Results correspond to GGA-BP calculations for the 39-atom cluster.

well as the associated value of the energy ΔE_0 for each one of the seven states. This relevant information is provided in Table I, where ΔE_0 is given taking as origin the reference configuration in O_h symmetry. Looking at Table I, it is worth remarking that the global minimum obtained in the present calculations corresponds to the $b_1(x^2-y^2)^1$ $a_1(3z^2-r^2)^2$ $b_2(xy)^2$ $e(xz,yz)^2$ configuration with $\Delta E_0=-0.71$ eV and $Z_{\mathrm{Fe}}^0=93$ pm. This fact thus supports that a Fe^+ impurity at a K^+ site moves spontaneously off center. Apart from this fact it should be noted that: (1) The ground state associated with the global minimum is *different* from $b_1^2a_1^2b_2^1e^2$ corresponding to $Z_{\mathrm{Fe}}=0$; (2) only a very small $\Delta E_0=-0.03$ eV value is found for the referred $b_1^2a_1^2b_2^1e^2$ configuration; and (3) among the seven considered electronic states there are two for which Fe^+ impurity remains on center.

More insight on these issues can be reached looking at Fig. 4, showing the calculated $E(Z_{\mathrm{Fe}})$ profiles of the total energy for four electronic configurations with $S=3/2$. As a salient feature it can be seen in Fig. 4 that $b_1^1a_1^2b_2^2e^2$ becomes the ground state after a relatively small off-center displacement of the Fe^+ impurity ($Z_{\mathrm{Fe}}=20$ pm). This change in the ground state is helped by the crossing of $b_1(\sim xy)$ and $b_2(\sim x^2-y^2)$ levels, which takes place during the off-center displacement (Fig. 2) and the small energy difference (0.06 eV) between $b_1^1a_1^2b_2^2e^2$ and $b_1^2a_1^2b_2^1e^2$ states obtained for $Z_{\mathrm{Fe}}=0$.

Up to now the off-center motion of Fe^+ in $\mathrm{KTaO_3}$ has been studied assuming—as a first approximation—that when Fe^+ moves from the K^+ site, the rest of ions are kept at their equilibrium positions for $Z_{\mathrm{Fe}}=0$. Seeking to explore whether this constraint substantially modifies the conclusions reached up to now, additional geometry optimizations on the $\mathrm{FeO_{12}Ta_8K_{18}^{47+}}$ cluster have also been performed. In these calculations the positions of *all* 13 ions in the $\mathrm{FeO_{12}^{23-}}$ complex have been optimized under the restriction of C_{4v} symmetry. Therefore, the complex can be described as $\mathrm{FeO_4O_4O_4^{23-}}$ thus involving three inequivalent planes of oxygen ligands which we denote as top, equatorial, and bottom according to their position along the z axis of Fig. 1. Let us first consider one of the oxygens in the top plane placed in $(a/2,0,a/2)$ when Fe^+ is on the center at (0,0,0). If the Fe^+ impurity moves upward along the [001] axis, the coordinates of the referred oxygen ion become equal to $(a/2\text{-}\Delta_t x,-\Delta_t y,a/2\text{-}\Delta_t z)$. The present calculations indicate that once the ligand relaxation is taken into account, $Z_{\mathrm{Fe}}=89.4$ pm while $\Delta_t z=1.1$ pm and $\Delta_t x=\Delta_t y=5.2$ pm. This implies a short inward relaxation of top ligands when Fe^+ approaches. Small changes are also found when considering the oxygens lying in the equatorial and bottom planes although such ligands experience a small outward relaxation when Fe^+ moves upward. For instance, oxygen ligands at $(a/2,a/2,0)$ and $(a/2,0,-a/2)$ under O_h symmetry move to $(a/2+\Delta_{\mathrm{eq}}x,a/2+\Delta_{\mathrm{eq}}y,\Delta_{\mathrm{eq}}z)$ and $(a/2+\Delta_b x,+\Delta_b y,-a/2+\Delta_b z)$. At equilibrium, it is found that $\Delta_{\mathrm{eq}}z=3.3$ pm, $\Delta_b z=0.9$ pm, $\Delta_{\mathrm{eq}}x=\Delta_{\mathrm{eq}}y=3.8$ pm, and $\Delta_b x=\Delta_b y=1.8$ pm. These results just stress that, for the present case, the ligand relaxation does not play a primary role for understanding the off-center motion of the Fe^+ impurity.

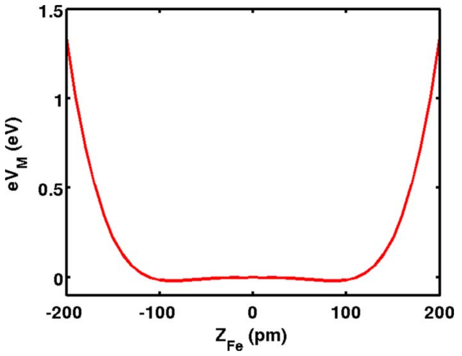

FIG. 5. (Color online) Electrostatic energy eV_M of the rest of lattice ions on the iron impurity with positive e ionic charge depicted along the [001] direction for the $\mathrm{Fe}_{\mathrm{K}}^{+}$ center.

Let us now shortly compare the present findings with those for $\mathrm{SrCl_2:Fe^+}$ where the existence of superhyperfine structure in EPR spectra has unambiguously proved the off-center shift of the impurity from the Sr^{2+} position.[44] In this case, it has been calculated (Ref. 29) $Z_{\mathrm{Fe}}=131$ pm thus implying that Fe^+ practically exhibits a square-planar coordination. This is not the case for Fe^+ in $\mathrm{KTaO_3}$ where $Z_{\mathrm{Fe}}=93$ pm is about half the distance between the impurity and the top plane of ligands ($a/2=199.4$ pm). This difference partially obeys the distinct structure of $\mathrm{SrCl_2}$ and $\mathrm{KTaO_3}$ host lattices. In the former case the first lattice cation in a $\langle 001\rangle$ direction next to a substitutional Fe^+ impurity lies at 696 pm while in the present case this value is equal only to 399 pm.

In a spontaneous off-center excursion of a given impurity, there is always a change in covalency with near ions, which is behind the required diminution of total energy. Despite this fact some insight can be obtained looking at the electrostatic potential V_M created by the rest of *point* ions on a rigid impurity. Obviously, the existence of an off-center shift along a given pathway is not favored in the regions where V_M increases steeply with Z_{Fe}. Bearing in mind this simple argument, the behavior of $e\{V_M(0,0,Z_{\mathrm{Fe}})-V_M(0,0,0)\}$ for the $\mathrm{Fe}_{\mathrm{K}}^{+}$ center along the Z_{Fe} distortion coordinate is portrayed in Fig. 5, where the (0,0,0) point corresponds to the on-center position. This potential has been derived by taking $+3e$, $-1.33e$, and $+1e$ for total charges on tantalum, oxygen, and potassium ions, respectively. We have verified that the form of $V_M(0,0,Z_{\mathrm{Fe}})$ is slightly dependent on the charges and thus practically the same profile is obtained using the nominal charges of involved ions.

It can be noticed that $V_M(0,0,Z_{\mathrm{Fe}})$ is essentially flat in the $0 < Z_{\mathrm{Fe}} < 100$ pm region while it behaves as a barrier for $Z_{\mathrm{Fe}} \geq 120$ pm. It is worth noting that the results of present calculations are consistent with the form of $V_M(0,0,Z_{\mathrm{Fe}})$ depicted in Fig. 5. Indeed the obtained equilibrium coordinate $Z^0_{\mathrm{Fe}} = 93$ pm places the Fe^+ impurity in the zone where $V_M(0,0,Z_{\mathrm{Fe}})$ is still flat.

C. *g* tensor of the Fe^{4}_{2} center

As pointed out in the Sec. I, the Fe^{4}_{2} center is characterized by an axial g tensor whose components for $S_{\mathrm{eff}} = 1/2$ are $g^{\mathrm{eff}}_{\perp} = 4.33$ and $g^{\mathrm{eff}}_{\parallel} = 2.02$.[10,12,14–16,18,22] If the spin of the ground state is $S = 3/2$, then the true values $g_{\parallel} = 2.02$ and $g_{\perp} = 2.16$ are thus derived from Eq. (1). Therefore, it turns out that $g_{\perp} - g_0$ is significantly higher than $g_{\parallel} - g_0$, a fact which is a fingerprint of the Fe^{4}_{2} center.[12,14] In the present study this tensor has been calculated by means of the ADF package at the equilibrium geometry corresponding to the $\mathrm{Fe}^{+}_{\mathrm{K}}$ center. The obtained values, $g_{\parallel} = 2.08$ and $g_{\perp} = 2.18$, are not unreasonable.

Let us now provide with a simple model for understanding why $g_{\perp} - g_0 > g_{\parallel} - g_0$. Figure 2 depicts the ground-state configuration corresponding to the equilibrium geometry of the $\mathrm{Fe}^{+}_{\mathrm{K}}$ center, where only the mainly d levels are portrayed. Excited states contributing to the g tensor in second-order perturbation also have $S = 3/2$. If only the main d levels in Fig. 2 are taken into account, such states involve an electron jump from a fully occupied level to a partially occupied level in the ground state. Among all possible excitations there are only 4 which fulfill these requirements. Such excitations can shortly be described as $xy \rightarrow x^2 - y^2$, $xy \rightarrow xz, yz$, $3z^2 - r^2 \rightarrow xz, yz$, and $3z^2 - r^2 \rightarrow x^2 - y^2$. Bearing in mind that for pure d-wave functions

$$\langle xy | l_z | x^2 - y^2 \rangle = 2i, \quad \langle xy | l_x | xz \rangle = -i,$$

$$\langle 3z^2 - r^2 | l_x | yz \rangle = -\sqrt{3} i, \quad \langle 3z^2 - r^2 | l_z | x^2 - y^2 \rangle = 0, \qquad (2)$$

it turns out that $g_{\parallel} - g_0$ is governed only by the $xy \rightarrow x^2 - y^2$ excitation while there are two excitations which contribute to $g_{\perp} - g_0$. Furthermore, as it has been emphasized in Sec. III B, the crossing of $b_1(\sim xy)$ and $b_2(\sim x^2 - y^2)$ levels takes place only at $Z_{\mathrm{Fe}} = 18$ pm. For $Z_{\mathrm{Fe}} \gg 20$ pm, the energy difference between the σ-antibonding $b_2(\sim x^2 - y^2)$ level and the π-antibonding $b_1(\sim xy)$ one increases very rapidly, following Z_{Fe}, as it is underlined in Figs. 2 and 4. More precisely, the corresponding difference of the one-electron energies $\varepsilon(x^2 - y^2) - \varepsilon(xy)$ is found to be equal to 1.1 eV for $Z_{\mathrm{Fe}} = 90$ pm. It should be stressed now that, at the equilibrium geometry, $\varepsilon(xz, yz) - \varepsilon(3z^2 - r^2)$ is found to be equal only to 0.2 eV. This simple fact already suggests that $g_{\perp} - g_0$ will be higher than $g_{\parallel} - g_0$. To be more specific, let us now write the expressions of $g_{\parallel} - g_0$ and $g_{\perp} - g_0$ derived only in second-order perturbations by means of Stone's formula.[45] If, as a first step, the covalency is not taken into account, $g_{\parallel} - g_0$ and $g_{\perp} - g_0$ are simply given by

$$g_{\parallel} - g_0 = \frac{8}{3} \frac{\xi}{E(xy \rightarrow x^2 - y^2)},$$

$$g_{\perp} - g_0 = 2 \frac{\xi}{E(3z^2 - r^2 \rightarrow xz, yz)} + \frac{2}{3} \frac{\xi}{E(xy \rightarrow xz, yz)}. \qquad (3)$$

Here ξ denotes the spin-orbit coefficient of Fe^+ while the denominators of Eq. (3) are the energies of involved excited states referred to that of the ground state. In the present case there are excitations whose energy is not always much higher. Although for this reason higher-order terms cannot be discarded for a quantitative understanding of the g tensor, Eq. (3) and the fact that $E(xy \rightarrow x^2 - y^2) \gg E(3z^2 - r^2 \rightarrow xz, yz)$ allow one to understand qualitatively a relevant experimental fingerprint of the Fe^{4}_{2} center.

IV. FINAL REMARKS

The present results underline the usefulness of *ab initio* calculations for clearing out the nature of transition-metal centers formed in oxides where EPR spectra do not show superhyperfine structure in samples not enriched with $^{17}\mathrm{O}$.

As the main conclusion of the study on the $\mathrm{Fe}^{5+}_{\mathrm{Ta}}$ center, it appears that a big off-center shift can hardly happen if the impurity has to move *against* one of the *closest* anions. Along this line recent experimental results have shown[46–48] that in the ferroelectric tetragonal phase of BaTiO_3, Ti^{4+} ions do not move off center along ⟨100⟩ directions toward oxygen ligands, as supposed in purely displacive models,[49] but they always displace along ⟨111⟩ directions in all phases including the cubic paraelectric phase.

It has been shown in this work that the K^+ site is more favorable than the Ta^{5+} site for the off-center motion of an impurity along a ⟨001⟩ direction in the KTaO_3 lattice. In agreement with this view, it has also been proved that Mn^{2+} impurities placed at the K^+ site of KTaO_3 (Ref. 19) and the Sr^{2+} site of SrTiO_3 (Ref. 24) experience off-center distortions.

The existence for the $\mathrm{Fe}^{+}_{\mathrm{K}}$ center of an excited state with $S = 3/2$ lying only ~ 0.2 eV above the ground state is strongly supported by the present results. Therefore, in spite of the fact that the spin-orbit constant $\xi = 0.04$ eV for free Fe^+ ion, the smallness of $E(3z^2 - r^2 \rightarrow xz, yz)$ is behind the significant anisotropy displayed by the true gyromagnetic tensor. Along this line the existence of this very low excitation is likely to be responsible for a zero-field splitting parameter D much higher than the typical Zeeman energy of $\sim 10^{-4}$ eV.[28] A calculation of the D parameter for both $\mathrm{KTaO}_3 : \mathrm{Fe}^+$ and $\mathrm{SrCl}_2 : \mathrm{Fe}^+$ systems is currently in progress.

Many authors have shown that spontaneous off-center displacements of impurities in solids result from the mixing of the ground state with appropriate excited electronic states by odd crystalline vibrations, displacing the impurity from the lattice point (pseudo Jahn-Teller effect).[29,35,36,50,51] The study performed in this work on different electronic configurations of the $\mathrm{Fe}^{+}_{\mathrm{K}}$ center demonstrates that an off-center displacement is a phenomenon extremely dependent on the electronic state and thus on the population of different one-electron levels. This behavior is shared by all instabilities driven by pseudo Jahn-Teller interactions.[29,52] Accordingly, a good understanding of the microscopic origin of the off-center shift corresponding to the Fe^{+}_{K} center in $KTaO_3$ requires to explore in detail the dependence on the distortion coordinate Z_{Fe} of all valence energy levels. The presence of three inequivalent planes of ligands when $Z_{Fe} \neq 0$ makes this study rather complex. Work along this relevant issue is now under way.

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