

## High magnetic anisotropy of Fe<sup>+</sup> ions in KTaO<sub>3</sub> and SrCl<sub>2</sub>

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The zero-field splitting constant,  $D$ , and the gyromagnetic tensor of the off-center systems KTaO<sub>3</sub>:Fe<sup>+</sup> and SrCl<sub>2</sub>:Fe<sup>+</sup> have been explored by means of calculations based on the density-functional theory at the  $C_{4v}$  local equilibrium geometry. The calculated  $D$  values for KTaO<sub>3</sub>:Fe<sup>+</sup> (9 cm<sup>-1</sup>) and SrCl<sub>2</sub>:Fe<sup>+</sup> (53 cm<sup>-1</sup>) are found to be much higher than typical figures measured for insulating compounds containing common 3d Kramers ions with a spin  $S > 1/2$  in the ground state. This result together with the calculated  $g_{\perp}$  and  $g_{\parallel}$  values concur with available experimental information. The high magnetic anisotropy derived for Fe<sup>+</sup> in KTaO<sub>3</sub> and SrCl<sub>2</sub> is shown to be strongly related to the existence of a <sup>4</sup>E excited state lying only at about 3000 and 600 cm<sup>-1</sup>, respectively, above the ground state. Implications of present findings in the search of new molecular magnets with high values of the magnetic anisotropy are discussed in some detail.

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### I. INTRODUCTION

A significant amount of work is currently focused on the properties of transition-metal (TM) impurities in insulating materials and in particular on those which are ferroelectric or display incipient ferroelectricity.<sup>1</sup> In this realm, the systems where the TM impurity does not remain at the substitutional position are specially interesting. In fact, when an off-center motion takes place in a cubic lattice it gives rise to the appearance of a local dipole moment. When such displacement is around 1 Å or even higher<sup>2,3</sup> this phenomenon implies a huge modification of the local symmetry which can, in turn, strongly affect all physicochemical properties associated with the impurity.<sup>4,5</sup> In particular, if the TM impurity has a spin  $S > 1/2$  the off-center displacement along the  $Z$  axis can induce a non-null zero-field splitting term in the *effective* spin Hamiltonian<sup>6</sup> which is written as

$$H_{\text{ZFS}} = D(S_Z^2 - S^2/3). \quad (1)$$

This term, which appears under an axial local symmetry but not in a cubic one, increases significantly the magnetic anisotropy of the ion.<sup>7</sup> Therefore, Kramers TM ions with a spin  $S > 1/2$  in the ground state, which undergo a big off-center motion are good candidates for displaying an unusually high magnetic anisotropy, a subject which is certainly of current interest in the realm of molecular magnets.<sup>8,9</sup>

Among the impurities investigated in the incipient ferroelectric KTaO<sub>3</sub> the unusual Fe<sup>+</sup> ion (3d<sup>7</sup> configuration) is particularly attractive for this goal. In fact, electron paramagnetic resonance (EPR) data<sup>10,11</sup> and recent theoretical calculations<sup>12,13</sup> support that such ion, found even in nominally pure samples, is not lying at the K<sup>+</sup> site of the KTaO<sub>3</sub> lattice but experiences an off-center excursion along a  $\langle 100 \rangle$ -type direction leading to a local  $C_{4v}$  symmetry (Fig. 1). The distance,  $Z_0$ , between the equilibrium position and the on-center one has been derived to be 93 pm from density-functional theory (DFT) calculations. Although up to now the actual value of the zero-field splitting constant  $D$  has not

been measured, a reasonable interpretation of available EPR data in the X band strongly suggests that  $D$  should be clearly higher than 0.3 cm<sup>-1</sup>.<sup>10-12</sup> A short discussion on this relevant issue is provided in Sec. II.

The existence of a  $D$  value much higher than  $\sim 1$  cm<sup>-1</sup> is, however, very unusual in the domain of 3d ions with half integer spin in insulating materials. Looking at available data of widely studied Kramers ions such as Cr<sup>3+</sup>, Fe<sup>2+</sup>, or Mn<sup>2+</sup> in *inorganic* compounds  $D$  is usually lying in the range  $10^{-2} - 1$  cm<sup>-1</sup>.<sup>6,14</sup> Only in the case of some biological compounds containing Fe<sup>3+</sup> values of  $D$  around 15 cm<sup>-1</sup> have been derived experimentally.<sup>15</sup> Despite this fact, a recent work carried out on Fe<sup>+</sup> in the insulating SrCl<sub>2</sub> lattice has shown that an off-center displacement of the iron ion from the strontium site ( $Z_0 = 1.3$  Å) leads to a  $D$  value close to 50 cm<sup>-1</sup>.<sup>16</sup> The microscopic origin of the off-center distortion in SrCl<sub>2</sub>:Fe<sup>+</sup> and KTaO<sub>3</sub>:Fe<sup>+</sup> has previously been analyzed in some detail.<sup>13,17</sup>

Bearing in mind these facts and also the current interest on atoms and ions displaying a huge magnetic anisotropy<sup>8,9,18,19</sup> this work is addressed, in a first step, to calculate the value of the zero-field splitting constant,  $D$ , and the gyromagnetic tensor,  $\mathbf{g}$ , corresponding to KTaO<sub>3</sub>:Fe<sup>+</sup> by means of *ab initio* calculations. It is worth noting that this task can now be carried out once the equilibrium geometry and the nature of the electronic ground state have both been reasonably established.<sup>12,13</sup> The calculation of the actual  $D$  value in KTaO<sub>3</sub>:Fe<sup>+</sup> is more complex than for SrCl<sub>2</sub>:Fe<sup>+</sup> where the active electrons are essentially *confined* in a small nearly square-planar FeCl<sub>4</sub><sup>3-</sup> unit.<sup>16,17</sup> This situation is, however, no longer true for KTaO<sub>3</sub>:Fe<sup>+</sup> partially because in KTaO<sub>3</sub> the band gap is only 3.6 eV while equal to 7.5 eV for SrCl<sub>2</sub>. Due to this fact it has been proved that in KTaO<sub>3</sub>:Fe<sup>+</sup> there is some bonding between Fe<sup>+</sup> and nearest tantalum ions and thus bigger FeO<sub>12</sub>Ta<sub>8</sub>K<sub>18</sub><sup>35+</sup> clusters have already been employed for exploring its properties.<sup>13</sup> Aside from providing with a reliable value for the zero-field splitting constant for KTaO<sub>3</sub>:Fe<sup>+</sup> we are particularly interested in clarifying

why this system as well as  $\text{SrCl}_2:\text{Fe}^+$  can have  $D$  values which are at least one order of magnitude bigger than those found for *usual* Kramers ions in inorganic compounds.

The present work is organized as follows. Section II is devoted to survey the experimental results which indirectly support the existence of a  $D$  value in  $\text{KTaO}_3:\text{Fe}^+$  well beyond  $0.3 \text{ cm}^{-1}$ . Main computational details are given in Sec. III while results derived for  $\text{KTaO}_3:\text{Fe}^+$  are given and compared to those obtained for  $\text{SrCl}_2:\text{Fe}^+$  in Sec. IV. Particular attention is paid to understand the main reasons behind the high- $D$  values found for both  $\text{KTaO}_3:\text{Fe}^+$  and  $\text{SrCl}_2:\text{Fe}^+$  systems. Some comments pointing out the relevance of present results in the search of molecular magnets with high anisotropy are addressed in the last section.

## II. SUMMARY OF PREVIOUS EXPERIMENTAL RESULTS

Experimental EPR data for  $\text{KTaO}_3:\text{Fe}^+$  look rather anisotropic.<sup>10,11</sup> When the applied magnetic field is parallel to a  $\langle 001 \rangle$  direction the two parallel and perpendicular signals are both *simultaneously* observed. This fact means that according to the cubic symmetry of the host lattice the principal symmetry axis (which appears as a result of the off-center motion of  $\text{Fe}^+$ ) can be one of the three  $\langle 100 \rangle$ ,  $\langle 010 \rangle$ , or  $\langle 001 \rangle$  main axes of the cube with equal probability. Similarly to what happens in the  $E \otimes e$  Jahn-Teller effect *random strains* are the final responsible for deciding which of the three principal axes of the cube is going to become the  $C_4$  axis for a *given*  $\text{Fe}^+$  center displaying a  $C_{4v}$  symmetry.<sup>20</sup>

From a *phenomenological* point of view the *observed* EPR signals associated with a  $\text{Fe}^+$  center can be described<sup>10,11</sup> by the simple effective spin Hamiltonian with axial symmetry

$$H_{eff}^* = g_{\parallel}^* \{S_Z^* H_Z\} + g_{\perp}^* \{S_X^* H_{X'} + S_Y^* H_{Y'}\}, \quad (2)$$

where the effective spin  $S^* = 1/2$  and the  $Z$  direction corresponds to the principal  $C_4$  axis of the center. What is relevant in the spin Hamiltonian embodied in Eq. (2) is that for a given orientation of the magnetic field,  $\mathbf{H}$ , there is only *one* EPR line observed for a given center. As regards the  $g_{\perp}^*$  and  $g_{\parallel}^*$  effective parameters which describe all the experimental EPR spectra of  $\text{KTaO}_3:\text{Fe}^+$  they have been reported to be  $g_{\perp}^* = 4.33$  and  $g_{\parallel}^* = 2.02$ .<sup>10,11</sup>

If, helped by the  $C_{4v}$  symmetry, the ground state of  $\text{Fe}^+$  in  $\text{KTaO}_3$  has no orbital degeneracy it is then hard to accept that the actual value of the spin,  $S$ , for such state is just  $S = 1/2$  and the associated gyromagnetic factor  $g_{\perp}$  more than twice the value corresponding to the free electron,  $g_0 = 2.0023$ . On this basis it has been argued that the spin for the ground state of  $\text{KTaO}_3:\text{Fe}^+$  is  $S = 3/2$  although *only* the transition  $|3/2; M_S = -1/2\rangle \rightarrow |3/2; M_S = +1/2\rangle$ , which is  $D$  independent, is actually observed by EPR.<sup>10</sup> A similar situation has been found for  $\text{SrCl}_2:\text{Fe}^+$ .<sup>17,21</sup> This idea would explain that the *available* experimental results can be described by Eq. (2) although the correct spin Hamiltonian is, in fact, given by

$$H_{eff} = \beta \{g_{\parallel} S_Z H_Z + g_{\perp} (S_X H_X + S_Y H_Y)\} + D \left\{ S_Z^2 - \frac{S^2}{3} \right\} \quad (3)$$

with  $S = 3/2$ .

Bearing in mind that a matrix element  $\langle 3/2; M_S = -1/2 | S_X | 3/2; M_S = +1/2 \rangle$  is *different* from  $\langle 1/2; M_S = -1/2 | S_X | 1/2; M_S = +1/2 \rangle$ , it is a simple matter to find the connection between  $\{g_{\perp}^*; g_{\parallel}^*\}$  and  $\{g_{\perp}; g_{\parallel}\}$  quantities which is just given by

$$g_{\perp}^* = (S + 1/2) g_{\perp}; \quad g_{\parallel}^* = g_{\parallel}. \quad (4)$$

Therefore, if  $S = 3/2$  the actual  $g_{\perp}$  factor would be equal to 2.17 which is already a reasonable value for a  $3d$  impurity with an orbital singlet ground state. This interpretation is reinforced by recent DFT calculations on  $\text{KTaO}_3:\text{Fe}^+$  which support beyond any doubt<sup>12</sup> that, similarly to what is found for  $\text{SrCl}_2:\text{Fe}^+$ ,<sup>17</sup> the ground-state spin is  $S = 3/2$ . According to this analysis the actual  $D$  value should be much higher than  $0.3 \text{ cm}^{-1}$  because the EPR transitions like  $|3/2; M_S = +1/2\rangle \rightarrow |3/2; M_S = +3/2\rangle$  are not detected in experiments on  $\text{KTaO}_3:\text{Fe}^+$  using the X band.<sup>10,11</sup>

## III. COMPUTATIONAL DETAILS

The calculation of the  $D$  value and the gyromagnetic tensor,  $\mathbf{g}$ , for  $\text{KTaO}_3:\text{Fe}^+$  requires to know first the equilibrium geometry and electronic configuration of the ground state. This matter has recently been solved by means of DFT calculations on clusters containing up to 39 ions.<sup>12</sup> In that work, it has been shown that clusters which do not include the closest tantalum ions do not provide with reliable results, a point due to the covalent interactions between  $\text{Fe}^+$  and  $\text{Ta}^{5+}$  ions. These interactions are also briefly discussed in Sec. IV A. For this reason, the calculated values of  $D$  and the gyromagnetic tensor have been carried out using a  $\text{FeO}_{12}\text{Ta}_8\text{K}_{18}^{35+}$  cluster.

A multireference DFT approach, based on multiplet structure, developed by Daul *et al.*,<sup>22-25</sup> was employed for the calculation of  $D$  in both systems. First, an *average of configuration* (AOC) calculation is performed. It consists of a spin-restricted DFT calculation in which each of the molecular orbitals with a mainly  $d$ -impurity character is populated with the same number of electrons, 1.4 in the present case. The Kohn-Sham orbitals obtained in this calculation are those best suited for a ligand field treatment.<sup>22</sup> After this step, the energies of all possible Slater determinants arising from the  $d^7$  configuration are calculated in an unrestricted non-SCF (without orbital relaxation) DFT procedure using the orbitals from the AOC step. These calculations can be automatically performed with the Amsterdam density functional (ADF, releases 2006 and 2007) code.<sup>26</sup> We employed two exchange-correlation functionals: the Vosko-Wilk-Nusair<sup>27</sup> one in the local density approximation (LDA) and the generalized gradient approximation (GGA) in its Becke-Perdew<sup>28</sup> form and introduced relativistic effects under the zero-order approximation (ZORA).<sup>29</sup> High-quality triple- $\zeta$  basis sets from the ADF database, as well as optimized basis sets for  $\text{Fe}^+$  ion using the XATOM program,<sup>30</sup> were used in this section. We have verified that both basis

sets lead to the same results. The energies of this set of Slater determinants are used to extract, using a fitting procedure, the parameters of the one-electron  $5 \times 5$  ligand field matrix as well as Racah's parameters, B and C. It is possible to obtain the energies of the Slater determinants from these parameters using ligand field theory, finding that the average deviation between them and the DFT energies is never larger than 3%. As a conclusion, it is possible to substitute the large number of Slater determinants (120 in the case of a  $d^7$  ion) by this small set of ligand field parameters. Finally, these parameters are used to build a configuration interaction (CI) matrix of a model Hamiltonian which includes both the ligand field and the spin-orbit operators. By doing so, we are able to take into account electron correlation, both dynamic, coming from the DFT exchange-correlation potential, and nondynamic, coming from the CI. After solving the CI problem a multiplet structure is obtained and the magnetic anisotropy energy (MAE) is taken as the energy difference between the two lowest  $E_{1/2}$  and  $E_{3/2}$  states. More details about this method can be found in the literature.<sup>22-25,31</sup>

In the case of  $\text{SrCl}_2:\text{Fe}^+$  a different and independent method has also been employed for calculating the  $D$  value.<sup>16</sup> In that procedure we use the complete-active-space-self-consistent-field technique corrected by multistate many-body second-order perturbation theory (MS-CASPT2) as implemented in the MOLCAS package<sup>32</sup> to calculate the electronic wave functions of the impurity center and evaluate the spin-orbit Hamiltonian. As active electrons of  $\text{Fe}^+$  in  $\text{SrCl}_2$  are highly localized<sup>16,17,33</sup> calculations have been carried out using only a  $\text{FeCl}_8^{7-}$  cluster embedded into *ab initio* model potentials<sup>34</sup> to mimic the bulk of the lattice. We have verified that results are essentially unmodified for a larger, 21-ion cluster ( $\text{FeCl}_8\text{Sr}_{12}^{7+}$ ) a fact which is in accord with the localized character of the unpaired spin density in  $\text{SrCl}_2:\text{Fe}^+$ . Further details of these calculations are given elsewhere.<sup>16</sup> Due to the high computational cost when the number of atoms increases, this procedure has not been applied to a  $\text{FeO}_{12}\text{Ta}_8\text{K}_{18}^{35+}$  cluster with 39 atoms.

## IV. RESULTS AND DISCUSSION

### A. Electronic states of $\text{KTaO}_3:\text{Fe}^+$ and $\text{SrCl}_2:\text{Fe}^+$ at the equilibrium geometry

For the sake of clarity let us briefly describe the equilibrium geometry and the associated electronic structure of  $\text{KTaO}_3:\text{Fe}^+$  calculated, in a first step, ignoring the effects of spin-orbit coupling. These results are also compared with those previously obtained for  $\text{SrCl}_2:\text{Fe}^+$ .<sup>16</sup>

According to experimental EPR results<sup>10,11</sup> and previous theoretical calculations<sup>12,13</sup> the  $\text{Fe}^+$  impurity in  $\text{KTaO}_3$  is not placed at the substitutional  $\text{K}^+$  site with perfect dodecahedral coordination. In fact it moves off-center along a  $\langle 100 \rangle$  direction ( $Z_0=93$  pm) thus lying between the top and equatorial oxygen planes shown in Fig. 1. This significant off-center displacement leads to an important modification of one-electron orbitals with respect to the ones for strict dodecahedral coordination. A qualitative picture of the disposition of mainly  $3d$  levels at the equilibrium geometry can also be found in Fig. 1.

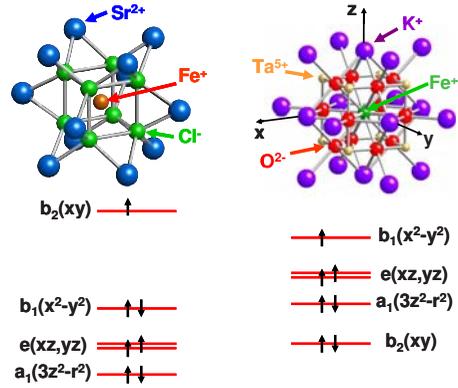


FIG. 1. (Color online) 21- and 39-ion clusters used to simulate, respectively, the  $\text{SrCl}_2:\text{Fe}^+$  (left) and  $\text{KTaO}_3:\text{Fe}^+$  (right) centers and their respective one-electron level diagrams for the mainly  $3d(\text{Fe})$  orbitals.

The relative position of the mainly  $3d(\text{Fe})$  orbitals at the calculated equilibrium geometry for  $\text{KTaO}_3:\text{Fe}^+$  is displayed in Table I where results derived for both  $\text{FeO}_{12}^{23-}$  and  $\text{FeO}_{12}\text{Ta}_8\text{K}_{12}^{35+}$  clusters are displayed. For comparison purposes the results obtained for  $\text{SrCl}_2:\text{Fe}^+$  are also included. Although for both  $\text{FeO}_{12}^{23-}$  and  $\text{FeO}_{12}\text{Ta}_8\text{K}_{12}^{35+}$  clusters the highest orbital is  $b_1(x^2-y^2)$  a relevant difference comes out when looking at the lowest one. Indeed, for the  $\text{FeO}_{12}^{23-}$  and  $\text{FeO}_{12}\text{Ta}_8\text{K}_{12}^{35+}$  clusters the lowest orbital is, respectively,  $a_1(3z^2-r^2)$  and  $b_2(xy)$ . This relevant fact stresses the role played by the empty  $5d(\text{Ta})$  orbitals whose mixing with the mainly  $xy$  orbital lowers its energy below all  $3d(\text{Fe})$  ones. This important point has been previously discussed in some detail.<sup>13</sup> Taking into account the scheme of energy levels depicted in Fig. 1 and the values gathered in Table I for the  $\text{FeO}_{12}\text{Ta}_8\text{K}_{12}^{35+}$  cluster the seven electrons of  $\text{Fe}^+$  lead to a  $(xy)^2(3z^2-r^2)^2(xz)^1(yz)^1(x^2-y^2)^1$  ground-state configuration with  $S=3/2$ . These results also suggest that a  ${}^4E$  excited state involving the  $3z^2-r^2 \rightarrow xz, yz$  excitation would only require a small energy of about  $3000 \text{ cm}^{-1}$ .

With regards to the  $\text{SrCl}_2:\text{Fe}^+$  system (Fig. 1) the calculated off-center displacement,  $Z_0=130$  pm,<sup>17</sup> is still higher than that found for  $\text{KTaO}_3:\text{Fe}^+$ . As it has previously been shown the associated electronic properties can essentially be understood considering only the nearly square-planar unit

TABLE I. Relative energies (in  $\text{cm}^{-1}$  units) of the mainly  $3d(\text{Fe})$  one-electron levels at the equilibrium position calculated for  $\text{KTaO}_3:\text{Fe}^+$  using  $\text{FeO}_{12}^{23-}$  and  $\text{FeO}_{12}\text{Ta}_8\text{K}_{18}^{35+}$  clusters. Calculations correspond to the equilibrium geometry obtained for the larger cluster. Values derived for  $\text{SrCl}_2:\text{Fe}^+$  are also shown for comparison purposes. The energy of the lowest one-electron orbital is taken as the reference in each case.

	$\text{FeO}_{12}^{23-}$	$\text{FeO}_{12}\text{Ta}_8\text{K}_{18}^{35+}$	$\text{SrCl}_2:\text{Fe}^+$
$a_1(3z^2-r^2)$	0	3704	0
$b_1(x^2-y^2)$	5338	8651	4250
$b_2(xy)$	2642	0	11520
$e(xz, yz)$	4579	6464	2170

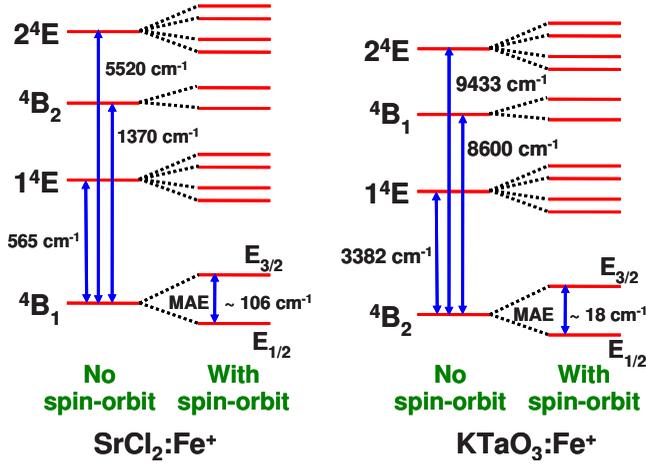


FIG. 2. (Color online) Diagrams for the low-energy multiplet states of  $\text{SrCl}_2:\text{Fe}^+$  (left) and  $\text{KTaO}_3:\text{Fe}^+$  (right) obtained through the multireference DFT method. For the present cases having  $S = 3/2$  the MAE is equal to  $2D$ .

$\text{FeCl}_4^{3-}$  formed as a result of the significant off-center excursion and neglecting the close  $\text{Sr}^{2+}$  ions.<sup>16,17</sup> At variance with what is found for  $\text{KTaO}_3:\text{Fe}^+$  the electronic properties are essentially unchanged on passing from a  $\text{FeCl}_8^{7-}$  cluster to a larger  $\text{FeCl}_8\text{Sr}_{12}^{17+}$  cluster. As the four  $\text{Cl}^-$  ligands of the  $\text{FeCl}_4^{3-}$  unit in  $\text{SrCl}_2$  are lying along  $\langle 110 \rangle$ -type directions (Fig. 1) the highest antibonding level is in this case  $b_2(xy)$ . The ground-state configuration in this system has been found to be  $(3z^2-r^2)^2(x^2-y^2)^2(xz)^1(yz)^1(xy)^1$  with  $S=3/2$ . The calculated values of one-electron energies,  $\varepsilon$ , for  $\text{SrCl}_2:\text{Fe}^+$  and its graphical scheme are, respectively, given in Table I and Fig. 1. It can be noticed that  $\varepsilon(xz, yz) - \varepsilon(3z^2-r^2)$  is around  $2000 \text{ cm}^{-1}$  and thus smaller than that found for  $\text{KTaO}_3:\text{Fe}^+$ .

Bearing in mind these results the energies of all 120 states emerging from a  $3d^7$  configuration have been calculated in order to elucidate the nature and energy of first excited states. Main results for both  $\text{KTaO}_3:\text{Fe}^+$  and  $\text{SrCl}_2:\text{Fe}^+$  systems are displayed in Fig. 2. It can be noticed that the first excited state for  $\text{KTaO}_3:\text{Fe}^+$  is found to be a  ${}^4E$  state lying  $3382 \text{ cm}^{-1}$  above the ground state while the energy of the second one,  ${}^4B_2$ , is equal to  $8600 \text{ cm}^{-1}$ . In the case of  $\text{SrCl}_2:\text{Fe}^+$  the energy of the first excited state,  ${}^4E$ , is found to be smaller than that for  $\text{KTaO}_3:\text{Fe}^+$  being equal only to  $565 \text{ cm}^{-1}$  while the second one,  ${}^4B_1$ , is calculated to be at  $1370 \text{ cm}^{-1}$ . The existence of a first excited state lying around  $1000 \text{ cm}^{-1}$  above the ground state is certainly unusual for common Kramers ions such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , or  $\text{Mn}^{2+}$  in inorganic materials.<sup>6,14</sup> As shown in the next sections this circumstance in  $\text{Fe}^+$  systems with  $C_{4v}$  symmetry is fundamental to enhance the magnetic anisotropy.

### B. Magnetic anisotropy and gyromagnetic tensor of $\text{Fe}^+$ in $\text{KTaO}_3$

The values of  $D$ ,  $g_{\perp}$ , and  $g_{\parallel}$  calculated for  $\text{KTaO}_3:\text{Fe}^+$  using the multireference DFT approach under LDA and GGA functionals are reported in Table II and compared with available experimental data. As shown in that table both

TABLE II. Values of  $g_{\perp}$ ,  $g_{\parallel}$ , and  $D$  for  $\text{KTaO}_3:\text{Fe}^+$  calculated by means of the multireference DFT method and the  $\text{FeO}_{12}\text{Ta}_8\text{K}_{18}^{35+}$  cluster. Results obtained for both LDA and GGA functionals are given and compared to available experimental data. The  $g_{\perp}$  and  $g_{\parallel}$  values both refer to the true spin  $S=3/2$  of the ground state. Experimental data come from Refs. 10 and 11.

	$g_{\perp}$	$g_{\parallel}$	$D$ ( $\text{cm}^{-1}$ )
LDA	2.23	2.09	8
GGA	2.25	2.09	9
Experimental	2.17	2.02	

functionals lead to practically the same results. The present calculations give rise to  $g_{\perp}=2.25$  and  $g_{\parallel}=2.09$  values both in qualitative agreement with experiments since  $g_{\perp} > g_{\parallel}$  and not far from the experimental ones,  $g_{\perp}=2.17$  and  $g_{\parallel}=2.02$ , although  $g_{\parallel}-g_0$  is somewhat overestimated. The comparison between experimental and calculated  $g_{\perp}$  and  $g_{\parallel}$  values given in Table II is not unreasonable. This fact supports that the actual value of  $D$  for  $\text{KTaO}_3:\text{Fe}^+$  would be around  $10 \text{ cm}^{-1}$  as derived from the present calculations thus implying that  $D$  is about thirty times bigger than the photon energy used in the X-band EPR experiments. Therefore, this result explains why EPR transitions like  $|3/2; M_S=+1/2\rangle \rightarrow |3/2; M_S=+3/2\rangle$  could not be detected in the experiments.<sup>10,11</sup>

### C. A simple model for understanding the $D$ value and gyromagnetic tensor of $\text{Fe}^+$ in $\text{KTaO}_3$

Seeking to clear out the actual origin of the high  $D$  value in  $\text{KTaO}_3:\text{Fe}^+$  and the main features displayed by its associated  $\mathbf{g}$  tensor a simple model is proposed founded on the following simplifying assumptions. (a) The effects of the spin-orbit coupling are included only at second-order perturbation level. (b) Only mixing of the ground state with the three lowest excited states of the  $3d^7$  configuration via spin-orbit interaction is taken into account. These states are depicted in Fig. 2 and its energies with respect to the ground state are designated by  $\Delta(1 {}^4E)$ ,  $\Delta(4B_1)$  and  $\Delta(2 {}^4E)$ . (c) The covalency involved in the five  $b_2(xy)$ ,  $a_1(3z^2-r^2)$ ,  $e(xz, yz)$ , and  $b_1(x^2-y^2)$  orbitals is neglected. (d) Excited states are approximated neglecting any configuration interaction. This means that excited states characterized by  $S=3/2$  and  $M_S=3/2$  are represented by a single Slater determinant.

For  $\text{KTaO}_3:\text{Fe}^+$  assumption (a) is not unreasonable as the spin-orbit coefficient,  $\xi$ , of free  $\text{Fe}^+$  ion is equal to  $356 \text{ cm}^{-1}$  and thus the ratio  $\xi/\Delta(1 {}^4E)$ , involving the first excited state, is around 0.1. Also, monovalent transition-metal cations exhibit a smaller covalency than more common trivalent or divalent species. For instance, 70% (80%) of the electronic charge in the  $b_1(x^2-y^2)$  [ $b_2(xy)$ ] orbital in  $\text{KTaO}_3:\text{Fe}^+$  is found to lie on iron, implying that assumption (c) is not unreasonable. Assumption (d) is the most drastic of the model as it neglects, for instance, the configuration interaction between  $1 {}^4E$  and  $2 {}^4E$  states. Bearing in mind this fact, the  $1 {}^4E$ ,  $4B_1$ , and  $2 {}^4E$  states are simply described by the following Slater determinants:

$$|1^4E\rangle = |xy\uparrow, xy\downarrow, 3z^2 - r^2\uparrow, xz\uparrow, xz\downarrow, yz\uparrow, x^2 - y^2\uparrow\rangle,$$

$$|4B_1\rangle = |xy\uparrow, 3z^2 - r^2\uparrow, 3z^2 - r^2\downarrow, xz\uparrow, yz\uparrow, x^2 - y^2\uparrow, x^2 - y^2\downarrow\rangle,$$

$$|2^4E\rangle = |xy\uparrow, 3z^2 - r^2\downarrow, 3z^2 - r^2\uparrow, xz\uparrow, xz\downarrow, yz\uparrow, x^2 - y^2\uparrow\rangle. \quad (5)$$

Looking at Fig. 1 these states arise from the one-electron excitations  $a_1(3z^2 - r^2) \rightarrow e(xz, yz)$ ,  $b_2(xy) \rightarrow b_1(x^2 - y^2)$ , and  $b_2(xy) \rightarrow e(xz, yz)$ , respectively.

It is worth noting that the ground state,  $4B_2$ , is coupled to  $4E$  states through  $L_x$  and  $L_y$  operators. This admixture due to spin-orbit coupling gives rise to a second-order contribution to  $g_\perp - g_0$ . On the contrary,  $4B_2$  is coupled to a  $4B_1$  state through  $L_z$  thus providing with a contribution to  $g_\parallel - g_0$ . Taking into account the assumptions of the model the obtained expressions for  $g_\parallel$ ,  $g_\perp$ , and  $D$  are given by

$$g_\parallel - g_0 = \frac{8}{3} \frac{\xi}{\Delta(4B_1)},$$

$$g_\perp - g_0 = 2 \frac{\xi}{\Delta(1^4E)} + \frac{2}{3} \frac{\xi}{\Delta(2^4E)},$$

$$D = \frac{\xi^2}{9} \left\{ \frac{3}{\Delta(1^4E)} + \frac{1}{\Delta(2^4E)} - \frac{4}{\Delta(4B_1)} \right\}. \quad (6)$$

The equations relating the  $\mathbf{g}$  tensor with  $\xi$  and the  $\Delta(1^4E)$ ,  $\Delta(4B_1)$ , and  $\Delta(2^4E)$  excitation energies were reported previously.<sup>12</sup> All the simple expressions embodied in Eq. (6) point out that  $4E$  excited states favor a positive  $D$  value while the coupling of the ground state with the  $4B_1$  state gives rise to a negative contribution to  $D$ . From the present model it can be expected that  $D > 0$  and at the same time  $g_\perp > g_\parallel$  since, according to Fig. 2,  $\Delta(4B_1)/\Delta(1^4E) = 2.5$ . Both facts are in qualitative agreement with experimental data and results of present calculations. Moreover, using Eq. (6) and the calculated values  $\Delta(1^4E) = 3382 \text{ cm}^{-1}$ ,  $\Delta(4B_1) = 8600 \text{ cm}^{-1}$ , and  $\Delta(2^4E) = 9433 \text{ cm}^{-1}$ , together with a reduced  $\xi = 300 \text{ cm}^{-1}$  value to account for covalency, it is obtained  $g_\perp = 2.20$ ,  $g_\parallel = 2.09$ , and  $D = 6 \text{ cm}^{-1}$ . This simple analysis stresses that lowering the energy of the first excited state  $1^4E$  together with a significant separation between this state and  $4B_1$  results in a positive zero-field splitting.

A relation between  $g_\perp - g_\parallel$  and  $D$  is obtained from Eq. (6)

$$D = \frac{\xi}{6} (g_\perp - g_\parallel). \quad (7)$$

This relation suggests that an increase in the  $\mathbf{g}$  tensor anisotropy favors higher values of  $|D|$ . A similar relation to Eq. (7) has been reported for  $\text{Cr}^{3+}$  impurities ( $3d^3$  configuration) in a distorted octahedral symmetry.<sup>35</sup> In these cases under a tetragonal perturbation the  $4T_2$  excited state in  $O_h$  symmetry is split in  $4B_2$  and  $4E$  states whose energies are  $\Delta(4B_2)$  and  $\Delta(4E)$ , respectively. Using a similar model to that of Eq. (6) the estimated  $D$  value for a  $\text{Cr}^{3+}$  impurity in a distorted octahedral environment can be written as

TABLE III. Values of  $g_\perp$ ,  $g_\parallel$ , and  $D$  for  $\text{SrCl}_2:\text{Fe}^+$  calculated using the multireference DFT method. Experimental  $g_\perp$  and  $g_\parallel$  data are given for comparison. The  $g_\perp$  and  $g_\parallel$  values both refer to the true spin  $S=3/2$  of the ground state. Experimental data come from Ref. 21.

	$g_\perp$	$g_\parallel$	$D$ ( $\text{cm}^{-1}$ )
Experimental	2.6	2.02	
LDA	2.8	1.90	53

$$D = \frac{4}{9} \xi^2 \left\{ \frac{1}{\Delta(4E)} - \frac{1}{\Delta(4B_2)} \right\} \approx \frac{4}{9} \xi^2 \frac{\Delta(4B_2) - \Delta(4E)}{(10Dq)^2}. \quad (8)$$

Therefore, even taking  $|\Delta(4B_2) - \Delta(4E)| = 4000 \text{ cm}^{-1}$ ,  $|D|$  values smaller than  $1 \text{ cm}^{-1}$  are expected if  $10Dq = 15000 \text{ cm}^{-1}$ .

#### D. Gyromagnetic tensor and magnetic anisotropy of $\text{Fe}^+$ in $\text{SrCl}_2$

Although the  $D$  value for  $\text{SrCl}_2:\text{Fe}^+$  was recently calculated<sup>16</sup> no information was given on the obtained gyromagnetic tensor and its comparison with experimental values. This issue is now dealt with in the present work.

In Table III are collected the calculated,  $g_\perp$ ,  $g_\parallel$ , and  $D$  values for  $\text{SrCl}_2:\text{Fe}^+$  using the multireference DFT approach. The experimental  $g_\perp$  and  $g_\parallel$  values<sup>21,33</sup> are also included in Table III for comparison purposes. It can first be noticed that the significant difference between the experimental  $g_\perp = 2.60$  and  $g_\parallel = 2.02$  values is reasonably reproduced by the present calculations. As the experimental difference  $g_\perp - g_\parallel = 0.58$  for  $\text{SrCl}_2:\text{Fe}^+$  is certainly bigger than the figure  $g_\perp - g_\parallel = 0.15$  measured for  $\text{KTAO}_3:\text{Fe}^+$  it can be expected a higher  $D$  value for the former system. As shown in Table III the  $D$  value calculated by means of the multireference DFT approach is found to be  $53 \text{ cm}^{-1}$ . A similar  $D$  value (equal to  $46.5 \text{ cm}^{-1}$ ) has been derived using the MS-CASPT2 method.<sup>16</sup>

According to the present arguments the very high  $D$  value obtained for  $\text{SrCl}_2:\text{Fe}^+$  is mostly due to the existence of a very low  $1^4E$  excited state lying *only* about  $600 \text{ cm}^{-1}$  above the  $4B_1$  ground state (Figs. 1 and 2) while the energy of the excited  $4B_2$  state is calculated to be around  $1400 \text{ cm}^{-1}$ . The key role played by the first excited state in  $\text{SrCl}_2:\text{Fe}^+$  has recently been demonstrated.<sup>16</sup> Indeed if in the diagonalization of the spin-orbit matrix the first excited state  $1^4E$  is removed the actual value of  $D$  is found to be only equal to  $-8 \text{ cm}^{-1}$ . This figure can thus be compared with a  $D$  value close to  $50 \text{ cm}^{-1}$  when the first excited state is taken into account.

It should be remarked now that although the  $g$  shifts observed in TM impurities in insulators with an orbitally singlet ground state have usually been explained<sup>6</sup> treating the spin-orbit coupling in second-order *perturbations* this approximation is certainly not valid for  $\text{SrCl}_2:\text{Fe}^+$ . In fact, if the first excitation is  $\Delta(1^4E) = 565 \text{ cm}^{-1}$  then the ratio  $\xi/\Delta(1^4E)$  is equal to 0.63 and a model similar to that devel-

oped in Sec. IV C is thus meaningless. In other words, when the spin-orbit coupling is accounted for it produces a strong coupling between the first ( $1^4E$ ) and the second ( $^4B_2$ ) excited states of the same order as the weak-field interelectronic Coulombic interactions. A simple way to show this strong coupling is to look at the calculated zero-field splitting in the  $^4B_2$  excited state. In a normal calculation  $D(^4B_2) = -22 \text{ cm}^{-1}$ . By contrast, when the  $1^4E$  state is discarded in the diagonalization of the spin-orbit operator  $D(^4B_2)$  becomes positive and equal to  $12.5 \text{ cm}^{-1}$ .

## V. FINAL REMARKS

This work has shown that two monomer systems involving the unusual  $\text{Fe}^+$  species display a magnetic anisotropy much higher than that measured for other  $3d$  ions such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , or  $\text{Mn}^{2+}$  in inorganic materials.<sup>6</sup> This fact obeys, on one hand, to the existence of a spontaneous off-center motion which breaks the local cubic symmetry on the  $\text{Fe}^+$  ion a situation which is thus different to that observed for  $\text{NaX}:\text{Fe}^+$  ( $X=\text{F}, \text{Cl}$ ) systems, where  $\text{Fe}^+$  remains at the substitutional position.<sup>36,37</sup> On the other hand, monovalent  $3d$  ions are less sensitive than trivalent or divalent species to the influence of the so-called crystal field.<sup>17</sup> This fact favors in turn smaller separations between mainly  $d$  orbitals and, consequently, a decrease of the energy of low-lying excited states.

The present results can be of interest in the realm of molecular magnetism<sup>8</sup> where efforts are currently focused in finding a molecule formed out of several  $3d$  centers with high values of the total spin of the ground state,  $S$ , and also of the associated magnetic anisotropy described by  $D(S_Z^2 - S^2/3)$ . In particular if  $|D|$  is high enough and  $D < 0$  the system can be prepared in a state  $M_S = S$  and remain in it for a long time. The existence of a big anisotropic barrier acts against both thermal activated and tunnelling processes that destroy the magnetization.<sup>9</sup> In recent years special attention has been paid to build bigger molecules with the hope that increasing the number of involved  $3d$  ions (and thus the value of  $S$ ) it would also help to increase the anisotropic barrier,  $B_A$ , for passing from the  $M_S = S$  state to  $M_S = S - 1$ . However, even though molecules with  $S$  values up to  $83/2$

have been obtained no improvement on the  $B_A$  value has actually been observed.<sup>38</sup>

This behavior can be explained if the zero-field splitting has a *local* character.<sup>39</sup> In other words the zero-field splitting term  $D(S_Z^2 - S^2/3)$  actually comes from  $\sum_i D_i (S_{iz}^2 - \frac{S_i^2}{3})$ , where the index  $i$  runs over all magnetic ions and  $S_i$  and  $D_i$  mean the local spin and zero-field splitting constant of the  $i$  ion. Bencini and Gatteschi<sup>40</sup> showed that  $D$  and  $D_i$  constants are related by

$$D = \sum_i d_i D_i, \quad (9)$$

where for a pure ferromagnetic state  $d_i$  coefficients are found to be

$$d_i = \frac{S_i(S_i - 1)}{S(S - 1)} \quad (10)$$

implying that when  $S \gg 1$   $d_i$  scales with  $S$  as  $S^{-2}$ . Accordingly, one finds that for a molecule formed by identical ions coupled ferromagnetically  $B_A$  is essentially determined by the magnetic anisotropy due to one monomer.

Thus, the present considerations point out that the best path to obtain a molecular magnet with higher values of the magnetic anisotropy would be to synthesize it using monomers with high values of the local zero-field splitting constants,  $D_i$ . The present work has shown that monovalent  $3d$  ions with spin  $S_i > 1/2$ , such as  $\text{Fe}^+$ , are good candidates to achieve this goal.

The high  $D$  values derived for  $\text{Fe}^+$  in both  $\text{SrCl}_2$  and  $\text{KTaO}_3$  host lattices are partially driven by the off-center distortion. The  $Z_0$  value can be modified by the application of uniaxial and hydrostatic pressures and, in the case of thin films, by external electric fields. These actions can in turn lead to significant changes of the zero-field splitting constant,  $D$ . This issue deserves further investigation which is now in progress.

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