

The giant magnetic anisotropy energy of Fe^+ ions in SrCl_2

Pablo Garcia-Fernandez,^{*a} Florian Senn,^b Claude A. Daul,^b Jose Antonio Aramburu,^a
Maria Teresa Barriuso^c and Miguel Moreno^a

We show that values of the magnetic anisotropy energy (MAE), which are about two orders of magnitude larger than the usual ones for transition metal cations in insulators ($\sim 0.01\text{--}1\text{ cm}^{-1}$), can be found for the less common ion Fe^+ . In $\text{SrCl}_2:\text{Fe}^+$, the MAE is 93 cm^{-1} when calculated using second-order perturbation multi-configurational calculations (CASPT2) while a similar value is found using multi-reference density functional theory (MR-DFT). This result is even larger than other recently reported giant MAEs for atoms on surfaces or magnetic clusters. The microscopic origin of this giant MAE is discussed in detail.

Materials with large magnetic anisotropy energies (MAE) are highly sought after due to their technological relevance.¹⁻³ The MAE describes the intrinsic tendency of the spin of a system to be aligned along particular spatial directions and imposes the temperature, with random fluctuations over time, at which the system becomes super-paramagnetic. In the case of isolated 3d ions with spin $S > 1/2$ the MAE is directly related to the zero-field-splitting (ZFS) term $H_{\text{ZFS}} = D(S_z^2 - 1/3 S^2)$ in the effective spin Hamiltonian^{4,5} and is equal to $2|D|$. In systems with a large, negative ZFS⁶ the ground state is bi-stable in "up" and "down" spin states at relatively high temperatures, leading to prospective applications in the fields of information storage¹ and quantum computing.⁷⁻⁹ Both applications require non-interacting magnetic particles that have a well defined magnetic axis due to a high MAE. Good candidates to build these materials are magnetic nanoclusters,⁷⁻⁹ nanowires¹⁰ or magnetic atoms placed on a crystalline surface.^{2,3,11} For example, a *giant* MAE of 72 cm^{-1} has been reported for a Co ion placed on a platinum (111) surface.² This value is much higher than ZFS parameter values, $|D|$, measured for *usual* Kramers ions in inorganic insulators involving *simple* anions like F^- , Cl^- or O^{2-} . In these cases, $|D|$ is typically found to be in the range $0.01\text{--}1\text{ cm}^{-1}$ for common impurities^{4,5,12} like Fe^{3+} , Cr^{3+} or Mn^{2+} . Understanding the origin of large ZFS is the key to designing better materials in these fields.

In this communication we show that much higher values of $|D|$, in competition with those obtained in magnetic clusters and atoms on surfaces, can be reached in the case of the less common $3d^7\text{ Fe}^+$ ion which is formed in halides or oxide lattices. More precisely, this work is focused on Fe^+ doped SrCl_2 , a system which has been explored in detail through

electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) techniques.^{13,14} These experimental data, as well as recent theoretical calculations,¹⁵ are consistent with a spin $S = 3/2$ for the ground state and a C_{4v} local symmetry which originates as a result of a *spontaneous* off-centre displacement of the Fe^+ ion along a $\langle 001 \rangle$ direction of the SrCl_2 lattice (Fig. 1), leading to the formation of a nearly square-planar FeCl_4^{3-} unit.¹³⁻¹⁵ As a salient feature, EPR experiments on $\text{SrCl}_2:\text{Fe}^+$ only detect the $|3/2; -1/2\rangle \rightarrow |3/2; 1/2\rangle$ transition,^{13,14} a result which supports a D value much higher than the Zeeman energy for the Q-band (1 cm^{-1}).¹⁵ This idea is consistent with the experimental $g_{\perp} = 2.60$ and $g_{\parallel} = 2.02$ values measured¹³ for $\text{SrCl}_2:\text{Fe}^+$, which exhibit a much higher anisotropy than that encountered for the $3d^3\text{ Cr}^{3+}$ impurity in oxides where $|g_{\perp} - g_{\parallel}|$ usually lies between 0.003 and 0.01.^{4,12} Moreover, the fact that the EPR signal in $\text{SrCl}_2:\text{Fe}^+$ is not reduced when approaching 4.2 K¹⁴ suggests that D should be positive. Another interesting aspect of large MAEs in off-center impurity sites is that these materials display a magnetoelectric effect similar to that of multiferroic systems¹⁶ since the direction of distortion and the magnetic easy-axis associated with it can be changed by applying electric fields.

Bearing in mind the experimental difficulties of measuring D for *isolated* Fe^+ ions in SrCl_2 , in this work we chose to predict its value from *ab initio* simulations. Since these calculations are unusual,^{17,18} we have decided to use two reliable methods based on very different approaches.

In the first one we use the complete-active-space-self-consistent-field (CASSCF) technique corrected by multi-state second-order perturbation theory (MS-CASPT2), as implemented in the MOLCAS package,¹⁹ to obtain reliable values of the energies and wavefunctions of all the electronic states arising from the d^7 configuration of Fe^+ in SrCl_2 . As active electrons

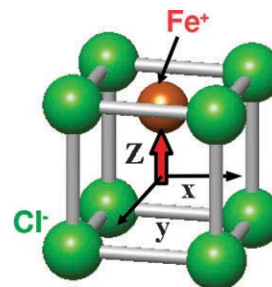


Fig. 1 Geometry of the $\text{SrCl}_2:\text{Fe}^+$ centre. The large arrow shows the off-centre displacement of the Fe^+ ion from the ideal cubic symmetry. Cartesian coordinates of the iron and representative upper and lower chlorine ions are $(0,0,1.26)\text{ \AA}$, $(1.69,1.69,1.75)\text{ \AA}$ and $(1.79,1.79,-1.76)\text{ \AA}$, respectively.

^a Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Avda. de los Castros s/n., 39005, Santander, Spain. E-mail: garciapa@unican.es

^b Département de Chimie, Université de Fribourg, Perolles, CH-1700, Fribourg, Switzerland

^c Departamento de Física Moderna, Universidad de Cantabria, Avda. de los Castros s/n., 39005, Santander, Spain

of Fe^+ in SrCl_2 are highly localized,^{14,15} the main calculations have been carried out using a FeCl_8^{7-} cluster embedded into *ab initio* model potentials (AIMPs)²⁰ to mimic the bulk of the lattice. We have checked that results are essentially unchanged for a larger, 21-ion cluster ($\text{FeCl}_8\text{Sr}_{12}^{17+}$). The ground state equilibrium geometry has been taken from a recent work¹⁵ and it is detailed in Fig. 1. The active space of the CASSCF calculations contains 9 orbitals: aside from the five orbitals stemming from the 3d levels of Fe^+ , those arising from 4s(Fe) and 4p(Fe) have also been considered. Their energies obey the rule of small 3d–4s (~ 1.8 eV) and 3d–4p (~ 3.4 eV) separations, a common situation when dealing with *monovalent* 3d ions. The atomic orbitals are represented by a large all-electron atomic natural orbital basis set,²¹ both for Fe (21s15p10d6f4g/8s7p6d2f1g) and Cl (13s10p4d/5s5p1d). This method is expected to be very accurate and has been applied to solids to calculate, *e.g.*, the exchange constant, J ,²² in KNiF_3 ²³ and, more recently, in CaCu_2O_3 ,²⁴ as well as in the calculation of small barriers among equivalent distortions in Jahn–Teller systems.^{25,26} It should be noted that in all these cases the spin–orbit coupling has not been included in the calculations, though it plays a key role in the present calculation of D . Here, the resulting CASSCF wavefunctions and MS-CASPT2 energies are employed to evaluate the spin–orbit Hamiltonian which is diagonalized to obtain the final energies. Similar approaches have been used, for example, in ref. 18 and references therein. In the present case the MAE is taken as the difference between the energies $E_{3/2}$ and $E_{1/2}$, corresponding, respectively, to the $\pm 3/2$ and $\pm 1/2$ Kramers doublets coming from the ground state (see Fig. 2). Our first method provides a splitting of 93 cm^{-1} , implying $D = 46.5\text{ cm}^{-1}$. Using the larger 21-ion cluster the splitting increases to 96 cm^{-1} , representing a variation of only 3%. Thus, the calculation of the MAE can be considered to converge with increasing cluster size.

The second method employed to derive the value of D for the nearly square-planar FeCl_4^{3-} unit is the multi-reference density functional theory (MR-DFT) of Daul *et al.*^{27,28} In this method, the energies of the 120 Slater determinants spanned by the d^7 configuration of Fe^+ are first evaluated using DFT and the energy of the corresponding microstates of the FeCl_4^{3-} unit is obtained from them. These DFT calculations

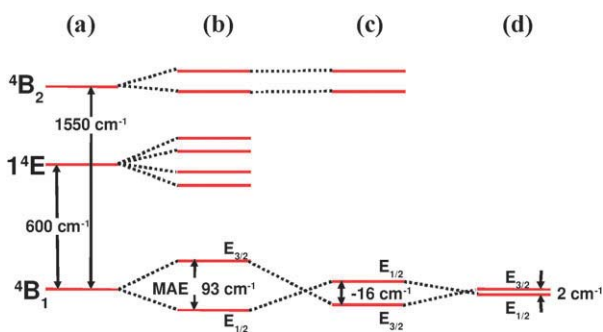


Fig. 2 Diagram showing the effect of the low-energy states over the MAE at the CASPT2 level. (a) Hamiltonian with only electrostatic terms (MAE not defined). (b) Full spin–orbit Hamiltonian evaluated with all d^7 states. (c) Results obtained with the full Hamiltonian when the 1^4E state is removed. (d) Results obtained with the full Hamiltonian when both the 1^4E and 4^4B_2 states are removed.

were performed with the Amsterdam density functional (ADF) program package (release 2007.01),²⁹ using the Perdew–Wang 91³⁰ generalized gradient approximation (GGA) for exchange–correlation functionals and basis-sets of triple- ζ quality, designed using the program XATOM.³¹ The potential of the rest of the lattice is simulated using point charges. In a subsequent step the configuration interaction (CI) matrix of a model Hamiltonian, including both the spin–orbit operator as well as the ligand field operator, is diagonalized to obtain the D value.²⁸ In this calculation a spin–orbit coupling constant ($\zeta_{3d}^{\text{SC}} = 365\text{ cm}^{-1}$), obtained from the CASSCF calculations, has been used. With this technique, described in detail in ref. 27, we calculate a MAE of 106 cm^{-1} .

Therefore, both procedures lead to a positive D value and a MAE close to 100 cm^{-1} for $\text{SrCl}_2:\text{Fe}^+$, a figure which is somewhat larger than the giant MAE of $\sim 72\text{ cm}^{-1}$ reported for a Co ion placed on a platinum (111) surface.² Along this line the MAE values derived for Mn_{12} and Fe_8 clusters from the superparamagnetic transition temperature are 46 cm^{-1} and 18 cm^{-1} , respectively.³² The value of $D = 46.5\text{ cm}^{-1}$ obtained for $\text{SrCl}_2:\text{Fe}^+$ can also be compared to the recent report by Hirjibehedin *et al.*³ of a large magnetic anisotropy ($D \sim 12\text{ cm}^{-1}$) found for an iron atom on top of a CN surface.

Let us now focus on the *microscopic origin* of the giant D value calculated for $\text{SrCl}_2:\text{Fe}^+$ which is at least 50 times larger than the largest values measured for Fe^{3+} , Cr^{3+} or Mn^{2+} in inorganic insulating materials.^{4,5,12} The ZFS parameter, D , of ions with $S > 1/2$ originates from the combined action of both spin–orbit coupling and axial distortion. Due to the spin–orbit coupling, the ground state with $S = 3/2$ can be mixed with excited states with the same spin but also with states of the d^7 manifold with $S = 1/2$. As a first step in our analysis, we have verified that the 80 states with $S = 1/2$ play a very minor role for understanding D . Indeed, when such states are removed in the diagonalization of the spin–orbit operator, the total MAE (93 cm^{-1}) reduces only by 0.3%. As the experimental spin–orbit parameter, ξ , of free Fe^+ ion is only equal to 356 cm^{-1} this result suggests that the high D value obtained for $\text{SrCl}_2:\text{Fe}^+$ should arise mainly from excited states with $S = 3/2$ lying only $\sim 1000\text{ cm}^{-1}$ above the ground state.

Ab initio calculations show that the ground state in $\text{SrCl}_2:\text{Fe}^+$ has 4^4B_1 symmetry in the C_{4v} point group. Its wavefunction can be described, in a first approximation, by the electronic configuration $(b_2)^1(e)^2(b_1)^2(a_1)^2$ (see Fig. 3). Taking into account that the spin–orbit operator spans the $E(1_x, 1_y)$ and $A_2(1_z)$ irreducible representations (irreps), the ground state can only couple to E and B_2 excited states. It is worth noting that the coupling to E and B_2 states leads to positive and negative contributions to D , respectively. The electronic states with $S = 3/2$ that can be obtained from the d^7 manifold of Fe^+ are (apart from the 4^4B_1 ground state): three E states (denoted as 1^4E , 2^4E and 3^4E) whose energies at the CASPT2 level are 600, 4400 and $13\,700\text{ cm}^{-1}$, respectively, two A_2 states at 6230 and $18\,750\text{ cm}^{-1}$ and a single B_2 (called 1^4B_2) state lying 1520 cm^{-1} above the ground state. On the other hand, all $S = 1/2$ states are found to have much larger energies than $S = 3/2$ states, the lowest being at $15\,630\text{ cm}^{-1}$. It is worthwhile to note that using the second method, based on

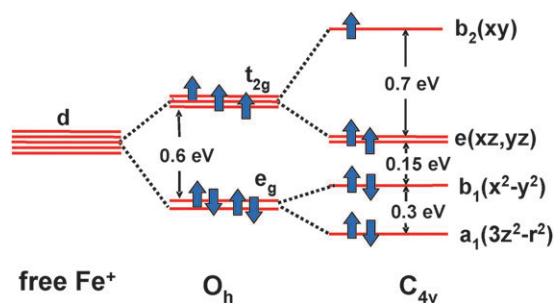


Fig. 3 Diagram showing the splitting of d-orbitals of Fe^+ in O_h and C_{4v} configurations and their occupations in the ground state.

DFT, the energy of the excitation to the 1^4E state is found to be equal to 565 cm^{-1} and thus in good agreement with the result of the CASPT2 calculation.

Among $4E$ and $4B_2$ states of the d^7 manifold it is particularly significant to underline the presence of 1^4E and 1^4B_2 states lying at *only* 600 and 1520 cm^{-1} , respectively, above the $4B_1$ ground state at the CASPT2 level. In order to quantify their importance in the MAE we have selectively removed them from the set of states used to diagonalize the spin-orbit operator. As indicated above, when all states of d^7 manifold are included in the diagonalization the MAE is 93 cm^{-1} ; however, when the 1^4E state is removed, the ZFS becomes *negative* and equal only to -16 cm^{-1} (Fig. 2c). Finally, when both the 1^4E and 1^4B_2 states are taken out of the calculation the ZFS becomes positive again and equal to 2 cm^{-1} (Fig. 2d). These results stress that the sign and the high D value derived for $\text{SrCl}_2:\text{Fe}^+$ strongly depend on the first excited state, 1^4E , lying only 600 cm^{-1} above the ground state, a situation which is not found for Fe^{3+} , Cr^{3+} or Mn^{2+} ions in inorganic insulators. On the other hand, the energy of the $4B_1 \rightarrow 1^4B_2$ excitation (inducing $D < 0$) is found to be 2.5 times higher than that for $4B_1 \rightarrow 1^4E$. A central question now is why this situation happens for Fe^+ in SrCl_2 and not for other impurities in simple crystals. To answer it let us consider the orbital diagram of the ground state shown in Fig. 3. In cubic symmetry the first excited state is $4T_2$ whose energy is equal to $10Dq$, a quantity which is well known to decrease when going from trivalent to monovalent ions. For $\text{SrCl}_2:\text{Fe}^+$, DFT calculations indicate that the $t_{2g}-e_g$ separation is 5200 cm^{-1} , a value which is certainly smaller than that found for the $3d^3\text{ Cr}^{3+}$ ion in oxides (around 17000 cm^{-1})¹² or chlorides (around 13000 cm^{-1}).³³

Let us now focus on the influence of the off-centre displacement of the Fe^+ ion upon electronic levels and states. Due to the formation of a nearly square-planar FeCl_4^{3-} unit the highest occupied antibonding level is $b_2(\sim xy)$ which is well separated from the other orbitals. More precisely, the energy difference between xy and $3z^2 - r^2$ one-electron levels is equal to 1.15 eV , while the one corresponding to $xz;yz$ and $x^2 - y^2$ is equal only to 0.15 eV (Fig. 3). As a simple description (without configuration interaction) 1^4E arises from the $x^2 - y^2 \rightarrow xz;yz$ excitation while 1^4B_2 originates from the $3z^2 - r^2 \rightarrow xy$ excitation. This argument suggests that $E(1^4E) < E(1^4B_2)$. Moreover, when working only in the d^7 manifold there are *two other* $4E$ states which lower the 1^4E energy through configuration interaction. By contrast, a parallel decrease of

energy cannot happen for 1^4B_2 as there is only one $4B_2$ state within the d^7 manifold. It should be remarked here that an additional and important reduction of the energy of 1^4E stems from the configuration interaction involving states where $4s$ and $4p$ orbitals of iron are occupied. This matter has been quantified by carrying out calculations where the $4s(\text{Fe})$ and $4p(\text{Fe})$ orbitals are excluded from the active space. In this case the ground state at the CASSCF level is $4B_1$ and its separation with the lowest $4E$ state is found to be 1550 cm^{-1} , while the MAE is reduced to 39 cm^{-1} . In the full CASPT2 calculations (that includes correlation between all electrons and orbitals) the excited state energy is corrected to 760 cm^{-1} and the MAE is 97 cm^{-1} . On the other hand, if both $4s(\text{Fe})$ and $4p(\text{Fe})$ orbitals are included from the beginning in the active space, the ground state at the CASSCF level is $4E$. This is corrected by the CASPT2 calculation that brings the $4B_1$ state to the final value of 600 cm^{-1} below 1^4E . These results stress the importance of electron correlation in the calculation of the MAE, in agreement with other studies,¹⁸ and in particular the key role played by low-lying $4s(\text{Fe})$ and $4p(\text{Fe})$ orbitals in $\text{SrCl}_2:\text{Fe}^+$. It is worth noting that these orbitals not only lower the energy of 1^4E but also favour the spontaneous off-centre distortion undergone by Fe^+ in SrCl_2 ¹⁴ which is responsible for the big difference between $\varepsilon(xy) - \varepsilon(3z^2 - r^2)$ and $\varepsilon(xz;yz) - \varepsilon(x^2 - y^2)$ outlined in Fig. 3. In fact, it has been shown that the vibronic admixture with the close $4s(\text{Fe})$ and especially $4p(\text{Fe})$ orbitals is an important channel favouring the off-centre motion of monovalent $3d$ ions.¹⁵ This idea is corroborated by the fact that among d^9 impurity ions in the CaF_2 lattice, only the monovalent Ni^+ ion goes off-centre while the divalent and *smaller* Cu^{2+} and Ag^{2+} ions remain at the on-centre position.³⁴

In this communication we have shown that the giant magnetic anisotropy found for Fe^+ in SrCl_2 is due to the particular electronic structure of this ion where very low excited states can appear. This is a consequence of both the very small value of $10Dq$ in hexahedral symmetry and the *large* off-centre displacement that breaks the initial cubic symmetry. The role of the off-centre displacement in $\text{SrCl}_2:\text{Fe}^+$ is somewhat similar to that played by a crystalline surface when a magnetic atom is placed on it.^{2,3} In one case, the anisotropy axis is placed along the off-centre distortion while in the other the axis is placed perpendicular to the surface. This behaviour has also been reported for others systems like Fe^+ in KTaO_3 ,^{35,36} where EPR data confirmed that D should again be much higher than 1 cm^{-1} .³⁵ Also, even though the value of D in $\text{SrCl}_2:\text{Fe}^+$ is positive, we have verified that the sign of D can be reversed when placing Fe^+ in a linear coordination. Work on these issues is now under way.

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