Mn$^{2+}$ impurities in fluoroperovskites: a test for theoretical calculations

**LETTER TO THE EDITOR**

# Mn²⁺ impurities in fluoroperovskites: a test for theoretical calculations

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**Abstract.**   The equilibrium impurity–ligand distance, $R_e$, in six fluoroperovskites of the AMF$_3$ series (A: K, Rb, Cs; M: Mg, Zn, Cd, Ca) doped with Mn²⁺ has been explored through density functional calculations for MnF$_6$A$_8$M$_6^{16+}$ clusters where the effects of the electrostatic potential due to the rest of the lattice are included. The $R_e$-values obtained coincide, within the experimental uncertainties, with those derived from the analysis of the experimental isotropic superhyperfine constant, $A_s$, and the $10Dq$-parameter and also with available extended x-ray absorption fine-structure results. This important result is shown to be practically independent of the quality of the basis set employed. From the analysis of recent electron paramagnetic resonance data for AlF$_3$:Mn²⁺ it is concluded that, for this system, $R_e \approx 197$ pm which is 7% smaller than the average distance for pure compounds involving MnF$_6^{4-}$ complexes. The latter figure is shown to be consistent with the substitution of Mn²⁺ for a trivalent cation in AlF$_3$:Mn²⁺. The present theoretical scheme has also been applied to Tl⁺ impurities in NaI. First results indicate an outwards relaxation of ligands which is equal to, at least, 5% and thus is much higher than the figure (1%) calculated by Aguado *et al* (Aguado A, Ayuela A, Lopez J M and Alonso J A 1998 *Phys. Rev.* B **58** 11 964).

## 1. Introduction

Knowledge of the right equilibrium distance, $R_e$, between a transition metal impurity in an insulating material and the nearest ions is a prerequisite for gaining a better insight into their associated properties [1, 2]. In addition to the energy of optical transitions, the Stokes shift or the spin-Hamiltonian parameters, the stability of a given impurity can also strongly depend on the local relaxation of close ions. This is for instance the case for Ag⁰ atoms in alkali halides formed after electron trapping by substitutional Ag⁺ impurities. The *electronic stability* of the centre formed in KCl after the electron capture has been shown [3] to be related to a huge outwards relaxation of six Cl⁻ ligands, though the precise $R_e$-value is not definitely clarified.

In the realm of impurities the determination of the right distance is not, however, a simple task, as standard diffraction methods cannot be used to achieve such a goal. As to the EXAFS technique, it requires a minimum of impurity concentration around 1% and the uncertainty in the $R_e$-values obtained is higher than 1 pm [4–6].

This situation can however be overcome through the analysis of *standard* optical and EPR parameters which can be measured for much lower impurity concentrations. For instance in the case of d⁵ [7–9], d⁷ [10] and d⁸ [11] ions in halide lattices with octahedral coordination it has been pointed out that $R_e$ can be derived from the experimental isotropic superhyperfine constant, $A_s$. The same procedure has been employed in the case of Jahn–Teller d⁹ ions

surrounded by four equivalent ligands displaying an elongated $D_{4h}$ geometry [12] and for $d^5$ ions in cubic or tetrahedral symmetry [7]. A general view of this method is given in reference [13].

In the case of TM impurities with local $O_h$ geometry, $R_e$-variations can also be extracted from the experimental $10Dq$-parameter [14–16], the energy of a charge-transfer transition [17] or the zero-phonon-line (ZPL) energy associated with a $10Dq$-dependent transition [18]. By means of the ZPL or the $A_s$-parameter detected by the ENDOR technique, changes in $R_e$ down to 0.05 pm can be detected [13, 18].

With the advent of more powerful theoretical methods based either on the *ab initio* Hartree–Fock (including CI) or in the density functional framework, one would expect that valuable information on the right impurity–ligand distance can also be reached from theoretical calculations on clusters centred around the impurity. As all calculations of this kind involve some approximations, it is crucial to verify the quality of the predictions made by a theoretical method for a given type of cluster. For achieving this goal, the set of $AMF_3$ cubic fluoroperovskites doped with $Mn^{2+}$ can certainly be useful. In fact *three different experimental* methods have previously been used for determining the right $R_e$-value in these systems. So for six such lattices the right $R_e$-value has been determined [7, 13] from the analysis of the experimental $A_s$-constant while for five of them it has also been obtained from the $10Dq$-parameter extracted from optical excitation spectra [14, 16]. Moreover for $KZnF_3$:$Mn^{2+}$ and $RbCdF_3$:$Mn^{2+}$ EXAFS measurements have also been carried out [19]. As shown in table 1 the $R_e$-values derived through the three different methods are coincident within the experimental uncertainty.

**Table 1.** Theoretical equilibrium distances, $R_e$, obtained through ADF calculations for $Mn^{2+}$-doped $AMF_3$ fluoroperovskites. ADF(IV) means that IV-type bases have been used for all of the atoms. In contrast, ADF(II) means that a IV-type basis has only been used for manganese while II-type bases have been used for the rest of the atoms. These $R_e$-values are compared to the figures obtained from the analysis of experimental $A_s$-parameters [7] and $10Dq$-parameters [14, 16] and also from that of available EXAFS data [19]. The experimental uncertainties are also indicated. For comparison purposes, the $M^{2+}$–$F^-$ distance of the perfect host lattice, $R_0$, is also given [29]. All the distances are in Å.

| Perovskites | $R_0$ | $R_e$ | | Experiment | | |
| | | ADF(IV) | ADF(II) | $10Dq$ | EXAFS | $A_s$ |
|---|---|---|---|---|---|---|
| $KMgF_3$:$Mn^{2+}$ | 1.987 | 2.057 | 2.058 | 2.068(4) | — | 2.07(1) |
| $KZnF_3$:$Mn^{2+}$ | 2.027 | 2.086 | 2.078 | 2.080(4) | 2.08(1) | 2.084(6) |
| $RbCdF_3$:$Mn^{2+}$ | 2.200 | 2.127 | 2.133 | 2.134(4) | 2.13(1) | 2.124(6) |
| $RbCaF_3$:$Mn^{2+}$ | 2.228 | 2.120 | 2.138 | 2.131(4) | — | 2.142(6) |
| $CsCdF_3$:$Mn^{2+}$ | 2.232 | 2.156 | 2.165 | — | — | 2.138(6) |
| $CsCaF_3$:$Mn^{2+}$ | 2.262 | 2.158 | 2.165 | 2.158(4) | — | 2.155(6) |

If the set of six fluoroperovskites doped with $Mn^{2+}$ (shown in table 1) is used for controlling the quality of a given method, the test is certainly very stringent. In fact, for reproducing reasonably well the $R_e$-values reached from the analysis of experimental data for the six systems of the series, the calculated $R_e$-value should involve an error less than 1% for *each member* of the series.

Throughout the present work, the $R_e$-value for the six systems given in table 1 is derived theoretically within the density functional framework applied to $MnF_6A_8M_6^{16+}$ clusters which include up to third neighbours of the impurity. A view of this cluster is given in figure 1. This study is founded on a recent one on $Cr^{3+}$ in a $K_3CrF_6$ lattice [20] showing that clusters of 21
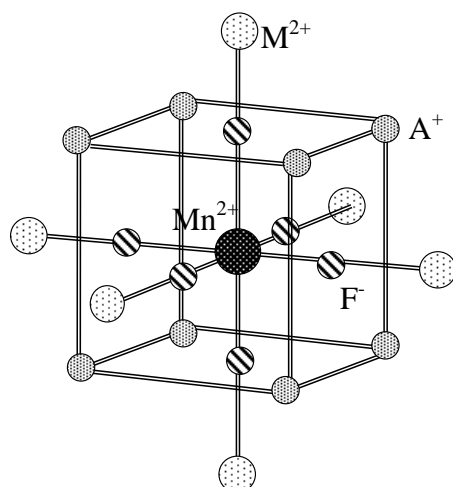
**Figure 1.** The cluster of 21 atoms used in the ADF calculation for $AMF_3$:$Mn^{2+}$ systems.

atoms centred at the $Cr^{3+}$ ion lead to $R_e$-values very close to experimental ones for fluoride compounds containing $CrF_6^{3-}$ units. Compared to the Hartree–Fock and the subsequent CI methodology, the DFT framework offers the advantage of a simpler inclusion of electronic correlation for the ground state [21] and a lower computational cost. Moreover, it has recently been pointed out [22] that DFT results are less sensitive to the quality of the basis set than in the case of *ab initio* calculations.

## 2. Theoretical analysis

Following previous results [20], $R_e$-values for the series of six $AMF_3$ fluoroperovskites doped with $Mn^{2+}$ have been obtained, calculating the energy of a $MnF_6A_8M_6^{16+}$ cluster as a function of the $Mn^{2+}$–$F^-$ distance, $R$, for the $^6A_1(t^3e^2)$ state. In that cluster, the $A^+$ and $M^{2+}$ ions are kept at their host lattice positions and thus only the $Mn^{2+}$–$F^-$ distance is left as variable. This assumption is reasonable provided that $u^1/R_0 \ll 1$ where $R_0$ is the M–F distance of the perfect host lattice and $u^1 = R_e - R_0$.

The calculations shown in this work have been performed using the Amsterdam density functional (ADF) code [23, 24]. For studying the influence of the quality of the basis set on the $R_e$-value, two types of basis set have been employed. Firstly, calculations have been carried out by means of functions of quality IV (which are implemented in the ADF code) involving triple-zeta basis functions plus a polarization function. In a second step, $R_e$ has also been computed using double-zeta functions of quality II for $F^-$ and $M^{2+}$ ions.

For $Mn^{2+}$, electrons up to the 3p shell are kept frozen and so are the 1s electrons of $F^-$. The $A^+$ and $M^{2+}$ ions are treated in a similar way. For instance, in the $RbCaF_3$ host lattice, electrons up to the 3d shell of Rb and the 3p shell of Ca are included in the core. Some calculations have also been made decreasing the number of frozen electrons in a given atom.

Calculations have been made in the framework of the generalized gradient approximation (GGA) by means of the Becke–Perdew functional, which uses Becke's [25] gradient correction to the local expression for the exchange energy and Perdew's [26] gradient correction to the local expression of the correlation energy. It is worth mentioning, however, that in the case of $Cr^{3+}$ in fluorides the $R_e$-values computed in the local density approximation (LDA) for a

21-atom cluster differ only by about 1% from those obtained through GGA [20]. The effects of the electrostatic potential due to the rest of the ions not included in the $MnF_6A_8M_6^{16+}$ cluster have been considered in all the calculations. When such a potential is not taken into account, the computed distances increase by about 1%. A similar situation is found in the case of $Cr^{3+}$ in elpasolites where a further analysis on this point is given.

## 3. Results and discussion

The equilibrium $Mn^{2+}$–$F^-$ distance, $R_e$, for the six $AMF_3$ fluoroperovskites containing substitutional $Mn^{2+}$ impurities obtained using basis functions of quality IV is reported in table 1. These results are essentially independent of the number of electrons included in the core. For instance, calculations on $ACaF_3$:$Mn^{2+}$ (A = Rb, Cs) where only electrons up to the 2p shell of Ca are included in the core have also been carried out. The values obtained differ from those derived including up to the 3p electrons of Ca in the core (table 1) by less than 0.25%. In table 1 the $R_e$-values obtained using basis functions of quality II for $F^-$ and $M^{2+}$ are also reported. It can be seen that the $R_e$-values obtained are practically unaffected by this reduction of quality in the basis set. This result thus concurs with those of a recent work [22] showing that DFT results are less sensitive to the quality of the basis set than in the case of *ab initio* calculations.

The calculated $R_e$-values for the six host lattices compare well with those derived from EXAFS measurements and the analysis of experimental $10Dq$- and $A_s$-parameters. In fact, for each lattice all of the $R_e$-values given in table 1 coincide taking into account the experimental uncertainties. From table 1 it can thus be inferred that the error involved in the calculated $R_e$ would be around 1 pm *for each one* of the six systems analysed. This result concurs with previous findings on $Cr^{3+}$ in halides [20] and also with recent results on the $HONO_2$ molecule obtained using *different* theoretical methods [27]. In the latter case the N–O distances corresponding to the $NO_2$ group are calculated with an error lying between 0.6 and 1 pm. The average error is of about 2 pm for the O–H bond and a bit higher for the distance between nitrogen and the oxygen atom of the OH group.

From inspection of table 1 it is seen that $|u^1/R_0|$ is always smaller than 4.5%. Let us designate as $R_e^3$ the true equilibrium $Mn^{2+}$–$M^{2+}$ distance between the impurity and the second neighbours in $\langle 100 \rangle$ directions and as $R_0^3$ the corresponding distance of the perfect host lattice. Following the theory of elasticity, it can be expected that if $|u^1/R_0| < 4.5\%$ then $|u^3/R_0^3| < 0.6\%$ where $u^3 = R_e^3 - R_0^3$. Therefore the neglect of the relaxation of second neighbours in $\langle 100 \rangle$ directions in the present calculation is reasonably justified *a posteriori* by this argument. It is worth recalling here that in the case of $CaF_2$:$Mn^{2+}$ there is an inward relaxation of $F^-$ ligands which has been measured through EXAFS [4] and the analysis of the experimental $A_s$-value [7]. From both methods it is found that $u^1/R_0 \approx -4\%$. Moreover, the analysis of EXAFS data indicates that the relaxation of nearest $Ca^{2+}$ ions is zero within the experimental uncertainties.

The equilibrium $V^{2+}$–$F^-$ distance, $R_e$, for three $AMF_3$ fluoroperovskites containing substitutional $V^{2+}$ impurities has recently been explored by means of *ab initio* calculations [28]. The values obtained for $KMgF_3$:$V^{2+}$ ($R_e = 2.074$ Å) and $CsCaF_3$:$V^{2+}$ ($R_e = 2.146$ Å) are close to the figures obtained for the same host lattices containing $Mn^{2+}$. At first sight this result looks reasonable bearing in mind that the ionic radius of $Mn^{2+}$ is only 4% higher than that of $V^{2+}$ [29].

Although the present calculations account for the experimental $R_e$-values of six $AMF_3$:$Mn^{2+}$ systems, *fine details* of their electronic structure cannot be so well reproduced using clusters of 21 atoms where surface effects are present. For instance in the Kohn–Sham $e_g$

orbital the electronic charge on the $M^{2+}$ ion is around 5%. In $RbCdF_3$:$Mn^{2+}$ such a figure would be smaller than the 1% obtained from experimental hyperfine data on the Cd nucleus [9, 30].

From the present results, reasonable information on the impurity–ligand distance in the case of insulating host lattices can be obtained through calculations for clusters in the DFT framework. This is particularly important in the case of impurities like $Tl^{2+}$, $Ni^+$ or $Ag^0$ which do not give rise to stable inorganic compounds. For KCl:$Tl^{2+}$ recent ADF results [31] lead to an $R_e$-value close to 2.75 Å. This figure has been shown to be consistent with that derived from the analysis of experimental charge-transfer transitions which are very sensitive to variations of the impurity–ligand distance [31].

Very recently, the lattice relaxation around the substitutional $Tl^+$ impurity in NaI has been investigated using the perturbed-ion method [32]. It has been found that the substitution of the diamagnetic $Tl^+$ ion for $Na^+$ leads to an outward relaxation of $I^-$ ligands, which is equal to only 1%. As this result is somewhat surprising in view of the difference between the ionic radii of $Na^+$ and $Tl^+$, ADF calculations on NaI:$Tl^+$ have also been undertaken. To this end, clusters of 33 and 81 atoms around the $Tl^+$ impurity have been used. First results obtained for *both* types of cluster indicate that $u^1/R_0 \geqslant 5\%$.

As indicated by the results displayed in table 1, when a $Mn^{2+}$ impurity is located inside an insulating host lattice, reasonable information on $R_e$ can be achieved from the analysis of the experimental $A_s$-parameter. The origin of the strong sensitivity of $A_s$- and $10Dq$-parameters to changes of the metal–ligand distance is discussed in reference [33]. In the case of fluoroperovskites the experimental isotropic superhyperfine constant goes from a value of $A_s = 40$ MHz for CsCaF$_3$:$Mn^{2+}$ to $A_s = 54$ MHz for KMgF$_3$:$Mn^{2+}$ [34]. Around $R = 212$ pm the $R$-dependence of $A_s$ [7] is described by

$$\mathrm{d}A_s/\mathrm{d}R = -1.6 \, \mathrm{MHz} \, \mathrm{pm}^{-1}. \tag{1}$$

Very recently the formation of substitutional $Mn^{2+}$ ions in the AlF$_3$ lattice has been demonstrated through the analysis of *powder* EPR spectra [35]. Such spectra reveal the existence of an isotropic superhyperfine interaction with six equivalent $F^-$ ions, $A_s$ being equal to 69 MHz. This figure is certainly higher than that measured for the series of $Mn^{2+}$-doped fluoroperovskites [34]. This relevant fact can be interpreted assuming an equilibrium distance in AlF$_3$:$Mn^{2+}$ smaller than in the cases of table 1. This idea is qualitatively reasonable because in the AlF$_3$ lattice the $Mn^{2+}$ impurity substitutes for a trivalent cation and not a divalent one like in the series of fluoroperovskites. As $R_0 = 1.79$ Å for the AlF$_3$ lattice is smaller than $R_0 = 1.99$ Å for KMgF$_3$, we can expect, in view of the results gathered in table 1, $R_e$ for AlF$_3$:$Mn^{2+}$ to be smaller than $R_e = 2.06$ Å derived for KMgF$_3$:$Mn^{2+}$ but higher than 1.79 Å. Assuming now equation (1), the difference between the experimental $A_s$-values of AlF$_3$:$Mn^{2+}$ and KMgF$_3$:$Mn^{2+}$ leads to $R_e = 1.97$ Å for the former system. Therefore in AlF$_3$:$Mn^{2+}$ the $Mn^{2+}$–$F^-$ distance would be closer to the $Fe^{3+}$–$F^-$ distance found in pure compounds involving $FeF_6^{3-}$ units [29] than to $R_e = 212$ Å which is the average value found for compounds containing $MnF_6^{4-}$ complexes. Cluster calculations are planned to support this idea.

In conclusion, the $R_e$-values for AMF$_3$:$Mn^{2+}$ systems measured by means of three different techniques are reasonably well reproduced by the present calculations. This opens the possibility of using this kind of methodology for determining the $R_e$-values for impurities like $Ag^0$, $Ni^+$ or $Cr^+$ in insulating lattices. Work in this direction is now under way.

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