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Determination of the Mn^{2+}-F^- distance from the isotropic superhyperfine constant for $[MnF_6]^{4-}$ in ionic lattices

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This paper is devoted to establish a quantitative nonempirical relation between the experimental isotropic superhyperfine constant A_s and the metal-ligand distance R for $[MnF_6]^{4-}$ placed in different ionic host lattices. By inspection of the theoretical molecular-orbital calculations performed on $[MnF_6]^{4-}$, it is proposed that λ_s, the $2s$ (F^-) admixture coefficient in the antibonding e_g^* orbital, is just given by cS_s where S_s is the corresponding group overlap integral while the value of the constant c, which is independent of R, should be close to 1.3. In a first step, we have determined R for Mn^{2+} in fluoroperovskite lattices from the experimental A_s values using a value $c=1.269\pm0.017$ derived from the NMR data for $KMnF_3$ and $RbMnF_3$. By means of this procedure, it is predicted that $R=2.084\pm0.11$ Å for $KZnF_3{:}Mn^{2+}$ and that $R=2.124\pm0.012$ Å for $RbCdF_3{:}Mn^{2+}$, which are in good agreement with recent extended x-ray-absorption fine-structure measurements on such systems. On the other hand, from the A_s values measured at room temperature and at 4.2 K, we have derived a thermal-expansion coefficient $\alpha=(17\pm5)\times10^{-6}$ K^{-1} for $[MnF_6]^{4-}$ in the $KZnF_3$ lattice which is comparable to the value $\alpha=16.52\times10^{-6}$ K^{-1} measured at 300 K for $RbMnF_3$. The present method gives also reasonable results for slightly distorted $[MnF_6]^{4-}$ clusters. In view of this, it is predicted that $R=2.126\pm0.012$ Å for the long Mn—F bond in K_2MnF_4. From this work, it is seen that if R_0 (which corresponds to the metal-ligand distance of the host lattice) is less than 2.10 Å, an outward relaxation occurs, whereas the opposite happens if R_0 is higher than 2.12 Å—a fact which is consistent with the mainly ionic bond between Mn^{2+} and F^-. Along this line of reasoning it is shown that a significant inwards relaxation $\Delta R/R_0=22.1\%$ ($\Delta R=R-R_0$) occurs for $RbF{:}Mn^{2+}$. The foundations of the method, which is able to detect changes in R down to about 2×10^{-4} Å, are thoroughly examined in this work. In particular, the possible influence of $1s$ core orbitals of F^- on the value of A_s is discussed: It is shown that for Mn^{2+}-doped fluoroperovskites better results are obtained when such a contribution is neglected.

I. INTRODUCTION

The properties due to a cationic impurity M in an ionic lattice can be understood in terms of the $[MX_n]$ cluster formed by the impurity M and the n-nearest anions X. Therefore, a good insight into the microscopic origin of such properties requires ascertaining the true M—X distance R, which may be very different from that corresponding to the perfect lattice R_0 in the case of substitutional impurities.[1,2]

Though this is a key problem to be solved for calculating the electronic levels of the $[MX_n]$ cluster in a given lattice or for understanding the variations undergone by the optical, magnetic, etc., properties associated to the impurity due to changes in the host lattice, the true value of R is very often unknown. This is mainly due to the lack of methods which enable one to obtain information about R from spectroscopic data. The advent of the sophisticated extended x-ray-absorption fine-structure (EXAFS) technique, however, makes it possible to measure R with accuracy, though large concentrations of impurity (more than 1%) are usually needed in the experiments.[3] This concentration of impurity is often not possible to reach and when it is, we must be sure that the impurity is dissolved in the host crystal and that precipitates or small aggregates are not formed.

Owing to this, it is thus desirable to obtain information about R from more conventional techniques which, moreover, can be sensitive to much smaller impurity concentrations. In this sense, for instance, a recent work[2] has shown the usefulness of the experimental ligand isotropic superhyperfine (shf) constant A_s for detecting outward ligand relaxation in Cu^0- and Ag^0-doped alkali halides.

In the same vein, the present work is devoted to determine R in systems in which Mn^{2+} is surrounded by an octahedron (regular or slightly distorted) of F^- ions through the experimental value of A_s.

Since the early work on Mn^{2+}-doped ionic fluoride lattices, the dependence of A_s with R (Refs. 4—8) was recognized and some quantitative relations between them have been proposed.[6,9-12] Nevertheless, these relations are empirical in the sense that they are not well founded from basic theoretical principles, and the parameters involved in such relations are considered to be purely fitting parameters. An example of this is given, for instance, by the recent work by Murrieta *et al.*[12] which introduces two empirical parameters in the assumed relation between A_s and R.

It is worth mentioning here that a similar attempt for deriving R from experimental data in the case of Mn^{2+}-doped fluoroperovskites has been carried out by Rubio *et al.*[11] through the analysis of the experimental a constant involved in the cubic term

$$\frac{a}{6}[S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S-1)(3S^2+3S-1)]$$

of the spin Hamiltonian of these systems. Such analysis was performed through an empirical expression in the framework of the superposition model and contains two adjustable parameters. Moreover it was assumed in such a work that $R=2.06$ Å for $KZnF_3$:Mn^{2+}. On the other hand, Rubio *et al.*,[11] using the R values calculated in this fashion, tried to explain the experimental A_s constants of Mn^{2+}-doped fluoroperovskites through a model founded in the work by Marshall and Stuart.[7] That model assumes that A_s is entirely due to the orthogonalization of $3d$ (e_g) orbital of Mn^{2+} to the $2s$ orbitals of the six nearest F^- anions. The $3d$ (e_g) orbital, however, is not necessarily that of free Mn^{2+}, but radial expansion effects are allowed. This effect is again accounted for by an empirical expansion parameter which is adjusted to the experimental results.

Though the A_s values calculated using this procedure reproduce, rather well, the experimental values for Mn^{2+} in fluoroperovskites, the model is founded on two assumptions which contrast with the results obtained through accurate molecular-orbital calculations for $[MnF_6]^{4-}$ (Refs. 13–18) and $[NiF_6]^{4-}$ (Refs. 18–22) clusters. (1) If we write λ_s, the $2s$ (F^-) admixture coefficient into the d (e_g) orbital of Mn^{2+} or Ni^{2+} as γ_s+S_s where S_s means the corresponding group overlap integral and γ_s is the covalent contribution, these calculations point out that γ_s/S_s is about 0.3.[17,19–21] This fact stresses that the covalent contribution to λ_s cannot be neglected in a quantitative interpretation of the experimental A_s value. (2) The expansion effects on the d (e_g) orbital of Mn^{2+} in $[MnF_6]^{4-}$ are negligible.[13–15] This fact is related to a $3d$-orbital population around 5.10,[16,18] very close to the value for free Mn^{2+}. A similar result is also found[21,22] for $[NiF_6]^{4-}$. This outlines that though the one-electron levels are actually modified by covalent admixture, the electronic charge transferred from ligands to the central ion is, however, very small for both $[MnF_6]^{4-}$ and $[NiF_6]^{4-}$ complexes.

The main goal of the present work is thus to discuss a new theoretical relation between λ_s and R, for systems involving the $[MnF_6]^{4-}$ cluster. Such a relation is founded on the theoretical calculations performed on the $[MnF_6]^{4-}$ cluster and, in particular, on that recently carried out by Emery *et al.*[17] for R varying between 1.9 and 2.3 Å. It is worth remarking here that this relation involves only one parameter which, moreover, can be derived from theoretical calculations. Therefore, no true empirical parameters are used in this work.

In the first step, the proposed relation between λ_s and R is used for deriving R from the experimental A_s value for Mn^{2+}-doped fluoroperovskites. In these cases, aside from $KMnF_3$ and $RbMnF_3$, where R is well known from crystal data, the value of R has been recently determined[23] by means of the EXAFS technique for $KZnF_3$:Mn^{2+} and $RbCdF_3$:Mn^{2+}, and a good test of the proposed relation between λ_s and R can be achieved.

Nevertheless, the connection between A_s and R depends on the relation between λ_s and A_s, which can be significantly affected by the possible influence of F^- $1s$ orbitals on A_s. This point which has been sometimes discussed in the literature[7,17,24] is also investigated through the present work.

Once the reliability of the present method has been analyzed, it is applied for measuring the thermal-expansion coefficient α for $[MnF_6]^{4-}$ in $KZnF_3$ and $KMgF_3$. This coefficient is compared to the experimental data obtained for $RbMnF_3$ through neutron-diffraction measurements.[25]

Our method is also applied to systems containing the $[MnF_6]^{4-}$ cluster slightly distorted from O_h symmetry. It will be shown that the predicted values for the two Mn—F distances in MnF_2, as well as for the short bond in K_2MnF_4, are in reasonable agreement with crystal data. Owing to this, we have determined by the present analysis the Mn—F distance of the long bond in K_2MnF_4 which is not known from x-ray diffraction data.

Finally, we have derived the Mn—F distances for Mn^{2+}-doped alkali fluorides from the experimental A_s value. These results point out that significant inward relaxation processes are involved in RbF:Mn^{2+} or KF:Mn^{2+}.

II. THEORETICAL

The $[MnF_6]^{4-}$ complex is a high-spin system whose ground state is $^6A_1$. The appearance of the isotropic superhyperfine constant A_s in the EPR spectrum of such a complex is essentially due to the hybridization of the d (e_g) orbitals of manganese with the s orbitals of F^- ligands. Thus the influence of fluorine core-polarization effects upon A_s is discussed later and it is shown to be negligible such as it usually happens for impurities with σ bonds surrounded by halide ligands.[26]

Within a molecular-orbital (MO) picture, the wave function of the antibonding e_g^* level is written as

$$|e_g^*\rangle=N[\,|d(e_g)\rangle-\lambda_{p\sigma}|\chi_{p\sigma}\rangle-\lambda_s|\chi_s\rangle]\,, \qquad (1)$$

where $|\chi_{p\sigma}\rangle$ and $|\chi_s\rangle$ mean symmetry-adapted linear combinations of ligand $p\sigma$ and s valence orbitals, respectively. In a weak bonding situation, such as that found in $[MnF_6]^{4-}$ or in $[NiF_6]^{4-}$, $N\simeq1$ and $\lambda_{p\sigma}^2$ and λ_s^2 are much smaller than the unity; $\lambda_{p\sigma}$ and λ_s are written as

$$\lambda_{p\sigma}=\gamma_{p\sigma}+S_{p\sigma},\quad \lambda_s=\gamma_s+S_s\ . \qquad (2)$$

Here, $S_{p\sigma}=\langle d(e_g)|\chi_{p\sigma}\rangle$ and $S_s=\langle d(e_g)|\chi_s\rangle$ are group-overlap integrals while $\gamma_{p\sigma}$ and γ_s are the so-called covalent contributions to $\lambda_{p\sigma}$ and λ_s, respectively.[19] In a weak bonding situation, $\gamma_{p\sigma}$ and γ_s are also the coefficients of the $|d\,(e_g)\rangle$ orbital in the mainly $2p\sigma$ (F^-) and $2s$ (F^-) e_g levels of the complex, respectively.[19]

In the case of the $p\sigma$ admixture, $\gamma_{p\sigma}$ is higher or comparable to $S_{p\sigma}$, while λ_s is dominated by the overlap contribution S_s.[17,19–21,24] This different behavior derives from the fact that while the 2p levels of F^- in an ionic lattice are close to the position of the 3d levels of the impurity ion, the 2s level of F^- is about 25 eV below the position of the 2p levels of F^-. Owing to this, the 2s admixture in $|e_g^*\rangle$ always has a perturbative character[26] and is thus dominated by the overlap contribution S_s, though γ_s is by no means negligible.

By contrast, the chemical bond is actually established through the p orbitals of F^-. Owing to this, the calculations by Emery *et al.*[17] for $[MnF_6]^{4-}$ and those by Shrivastava[27] for $[CuF_6]^{4-}$, both performed for several values of R, point out that the curve $\lambda_{p\sigma}^2(R)$ has a flat minimum, a fact which has actually been related to the stability of the chemical bond formed in the complex. In the case of $[MnF_6]^{4-}$, this flat minimum is found[17] for $R \simeq 2.15$ Å which is very close to the sum of ionic radii of Mn^{2+} and F^-. Moreover, the calculations by Emery *et al.*[17] clearly illustrate that $\lambda_{p\sigma}(R)$ does not follow $S_{p\sigma}(R)$, because in some regions $\gamma_{p\sigma}(R)$ decreases slightly when R decreases in order to allow the existence of such a minimum. A similar behavior has been suggested for $\gamma_{p\sigma}(R)$ in the case of Ag^0-doped NaCl and KCl in order to explain the small variations undergone by the anisotropic shf tensor of these systems.[2] These facts indicate that the variation of $\lambda_{p\sigma}$ with respect to R is not simple to predict, while that of λ_s appears to be much simpler.

Furthermore, the work of Emery *et al.*[17] on $[MnF_6]^{4-}$ shows that λ_s/S_s is nearly constant in the range $1.9 < R < 2.3$ Å in which the calculations were performed. In fact, such MO calculations predict that λ_s/S_s varies from 1.27 for $R = 1.9$ Å to 1.37 for $R = 2.3$ Å; therefore, a variation of only 8% when R increases 0.4 Å is implied. Moreover, the same $\lambda_s(R)$ curve is theoretically predicted for $[MnF_6]^{4-}$ either using a Sugano-Shulman approach or by means of a simplified Hartree-Fock-Roothaan procedure.[17]

It is worth mentioning here that the calculations performed on $[NiF_6]^-$ give λ_s/S_s values which are also close to 1.3.[19–21]

These features can be roughly understood assuming the Wolfsberg-Helmholz hypothesis[28] which makes the nondiagonal elements h_{ij} of the secular equation equal to $\frac{1}{2}K(h_{ii}+h_{jj})S_{ij}$. If we apply this guess to the present case taking $K = 2$ (Ref. 29) it is found that

$$\lambda_s \simeq \left[1 - \frac{h_{dd}}{h_{dd}-h_{ss}} \right] S_s \ , \tag{3}$$

where h_{dd} and h_{ss} are the diagonal matrix elements corresponding to the d orbital of Mn^{2+} and to the s orbital of F^-, respectively. Now taking $h_{dd} \simeq -10$ eV and $h_{ss} \simeq -40$ eV, it is typically[17,19] found that λ_s/S_s is about 1.3. On the other hand, the substantial difference existing between h_{dd} and h_{ss} makes the relation γ_s/S_s rather insensitive to changes experienced by both h_{dd} and h_{ss} due to variations in R.

The preceding arguments lead us to propose that the relation between $\lambda_s(R)$ and $S_s(R)$ is a constant, denoted by c, which is independent of R at least in a good first approximation. In other words, our main assumption is given by

$$\lambda_s(R) = cS_s(R) \ . \tag{4}$$

Moreover, if we take into account the MO calculations on $[MnF_6]^{4-}$ and $[NiF_6]^{4-}$ this constant c should be close to 1.3. This is the basic point for our subsequent analysis of the experimental A_s constant, in order to deduce from it the true value of the Mn—F distance R.

Regarding the value of $S_s = \langle d\ (e_g) | \chi_s \rangle$ it could be affected, in principle, by expansion effects on the $d\ (e_g)$ function of manganese. Thus the self-consistent field (SCF) calculations performed on $[MnF_6]^{4-}$ indicate[13–15] that such effects do not exist in practice upon the $d\ (e_g)$ function in $[MnF_6]^{4-}$. In particular, the SCF calculations quoted by Lohr[15] point out that the increase of S_s due to the expansion of the $d\ (e_g)$ wave function is less than 0.3%. A similar situation[21,22] is encountered in the SCF calculations on $[NiF_6]^{4-}$. Owing to this, the group-overlap integrals S_s will be calculated through this paper using accurate Roothaan-Hartree-Fock wave functions of free Mn^{2+} and F^- ions.[30] Once a reliable relation between λ_s and $S_s(R)$ has been established, it is necessary to relate λ_s to A_s in order to connect the experimental value A_s with R.

Through this work, two situations will be studied. In the first one, labeled model I, we shall assume that A_s is entirely due to bonding with the 2s orbital of F^-. On the other hand, in the second one, denoted model II, we shall take into account the possible influence of the core 1s orbital of F^- on A_s. Therefore, model I gives rise to the following relation between A_s and λ_s for weak bonding cases:

$$A_s = \tfrac{1}{3}\lambda_s^2 \frac{A_{2s}^0}{2S} \ , \tag{5}$$

where

$$A_{2s}^0 = (8\pi/3)2g_N\beta\beta_N \, |\psi_{2s}(0)|^2$$

and $S = \frac{5}{2}$ for the ground state of $[MnF_6]^{4-}$. In the case of F^-, $A_{2s}^0 = 14\,978 \times 10^{-4}$ cm^{-1}. It must be stressed here that relations equal or similar to Eq. (5) have been usually postulated in order to derive MO coefficients from the experimental shf tensor of impurities or defects. In contrast, the inclusion of core s orbitals of the ligand in the interpretation of the experimental A_s value has rarely been taken into account.[24]

As the 1s orbital of free F^- ion is 637.4 eV below the position of the 2s orbital, it is thus very reasonable to assume that the admixture of the 1s orbitals of F^- into $|e_g^*\rangle$ comes only from orthogonalization. Owing to this, the relation between A_s and λ_s in a weak bonding situation for model II will be as follows:

$$A_s = \tfrac{1}{3}\lambda_s^2 \frac{A_{2s}^0}{2S} \left[1 - \frac{S_{1s}\psi_{1s}(0)}{\lambda_s \psi_{2s}(0)} \right]^2 , \tag{6}$$

$\psi_{1s}(0)/\psi_{2s}(0)$ being 4.43 for free F^-.[30] Thus λ_s derived from the experimental A_s value will be higher for model II than for model I. This point has been explained with more detail by Owen and Thornley,[24] for instance.

Let us now discuss the possible influence of core-polarization effects in $[MnF_6]^{4-}$ on the experimental A_s value. The work by Harvey *et al.*[31] stresses that such effects give rise to an isotropic hyperfine constant $A_{cp}^{0}=101\times10^{-4}$ cm^{-1} for the ground state of the fluorine atom.

If we roughly assume that the core-polarization contribution to A_s in $[\mathrm{MnF}_6]^{4-}$ is given by the total unpaired p electron spin density on a fluorine ion multiplied by $A_{cp}^{0}/2S$ (with $S=\frac{5}{2}$ for the present case) such a contribution would be given by $(f_\sigma+2f_\pi)A_{cp}^{0}/5$, where, as usual, $f_\sigma=N^2\lambda_{p\sigma}^2/3$ and $f_\pi=N^2\lambda_\pi^2/4$.

The neutron data on MnF_2 give $f_\sigma+2f_\pi+f_s=3.3\%$ for this compound, while the NMR data for RbMnF_3 and KMnF_3 give values of f_s near 0.5% and values of $f_\sigma-f_\pi$ near 0.3%.[17] Therefore, assuming $f_\sigma\simeq1.1\%$ and $f_\pi\simeq0.8\%$, we find a typical value $(f_\sigma+2f_\pi)A_{cp}^{0}/5\simeq0.6\times10^{-4}$ cm^{-1}, which is indeed much smaller than the experimental A_s values found for $[\mathrm{MnF}_6]^{4-}$ complexes typically around 15×10^{-4} cm^{-1}. Moreover, as 0.6×10^{-4} cm^{-1} lies within the experimental error of A_s for some of the studied cases in the next sections, we shall neglect core-polarization effects on A_s through the present study.

III. Mn^{2+} IN FLUOROPEROVSKITES

A. Model I

The isotropic shf constant A_s has been measured for a large number of fluoroperovskites lattices containing Mn^{2+} (Table I). If Mn^{2+} is dissolved in a host lattice, then the measurements of A_s are made by means of EPR or electron-nuclear double resonance (ENDOR) studies. If Mn^{2+} is a cation of the fluoroperovskite lattice, however, A_s can be determined through fluorine NMR. This is an additional advantage with respect to the use of the "*a*" parameter for determining R. In fact, such a parameter cannot be measured by EPR when Mn^{2+} enters as a component of a perfect lattice.

Owing to this we have first calculated the c constant involved in the present method using the experimental values of A_s obtained for KMnF_3 and RbMnF_3 for which R is well known. By taking into account Eqs. (4) and (5) of model I and the experimental errors of A_s for both cases, it is found that $c=1.269\pm0.017$, which is quite consistent with the calculations by Emery *et al.*[17] on $[\mathrm{MnF}_6]^{4-}$ in the range $1.9\leq R\leq2.3$ Å. Next, we have derived the values of R for Mn^{2+}-doped fluoroperovskites using model I. These results are collected in Table I and compared to the recent EXAFS measurements for KZnF_3:Mn^{2+} and RbCdF_3:Mn^{2+} as well as to the estimations made of Rubio *et al.*[11] through the analysis of the experimental a parameter.

The main fact demonstrated in Table I is the excellent agreement existing between the values of R predicted through model I for KZnF_3:Mn^{2+} and RbCdF_3:Mn^{2+} and those obtained by means of EXAFS measurements. This gives great support to the present estimations of R for the other cases of Table I using model I.

In particular, these results outline that though R_0 varies from 1.993 (for KMgF_3) to 2.262 Å (for CsCaF_3), the corresponding R values go only from 2.07 to 2.15 Å. Moreover, Table I indicates that if $R_0\gtrsim2.12$ Å, then the intro-

TABLE I. Values of R derived from the experimental A_s constant for Mn^{2+} in fluoroperovskites using model I [Eq. (4)] with $c=1.269\pm0.017$ and model II [Eq. (6)] with $c=1.593\pm0.017$. All the A_s values reported here have been performed at room temperature except for KCdF_3:$\mathrm{Mn},^{2+}$ which was made at 550 K.

Lattice	R_0 (Å)	A_s (experiment) (10^{-4} cm^{-1})	Reference	R (Å) (model I)	R (Å) (model II)	R^a (Å)	R^b (Å)
KMgF_3	1.993	18.1 ±0.7	4	2.070±0.020	2.043±0.017		2.056±0.009
KZnF_3	2.026	17.3 ±0.2	9	2.084±0.011	2.067±0.012	2.08±0.01	2.061
KMnF_3	2.095	16.3 ±0.4	6	2.099±0.015	2.098±0.013		
RbMnF_3	2.120	15.7 ±0.7	32	2.112±0.020	2.116±0.016		
KCdF_3	2.145	15.4 ±0.3	9	2.115±0.012	2.125±0.011		2.104±0.009
TlCdF_3	2.197	14.8 ±0.3	9	2.126±0.012	2.147±0.012		2.115±0.008
RbCdF_3	2.200	14.9 ±0.3	9	2.124±0.012	2.146±0.012	2.13±0.01	2.112±0.008
RbCaF_3	2.228	13.95±0.3	9	2.142±0.013	2.167±0.012		2.138±0.008
CsCdF_3	2.230	14.15±0.3	9	2.138±0.013	2.165±0.011		
CsCaF_3	2.262	13.25±0.3	9	2.155±0.013	2.186±0.013		

[a] Values compared to the EXAFS measurements by Leblé (Ref. 23).

[b] Values compared to the estimations by Rubio *et al.* (Ref. 11) from the experimental a constant.

duction of substitutional Mn^{2+} gives rise to an inwards ligand relaxation while the opposite occurs for $R_0 \lesssim 2.10$ Å. This behavior is quite consistent with the mainly ionic character of bond in perovskites, which suggest that the Mn—F distance should tend to be near the sum of ionic radii of Mn^{2+} and F^- whose value $R_0(\text{Mn—F})=2.13$ Å. Furthermore, the calculations by Emery *et al.*[17] give a flat minimum in the $\lambda_{p\sigma}^2(R)$ curve for R about 2.15 Å.

It can also be noted from Table I that though the true Mn^{2+}—F^- distances can be rather different from R_0, the R values are ordered in the same way as those of R_0 corresponding to the host lattices. This behavior has also been observed for Cu^0 and Ag^0 in alkali chlorides.[2]

With regard to the values of R derived by Rubio *et al.* from their empirical analysis of the a parameter,[11] they exhibit similar trends to those obtained in the present work, though small differences appear in the predicted values of R. In particular, they assumed $R=2.061$ Å for $KZnF_3$:Mn^{2+}, which is slighly smaller than the value $R=2.08\pm0.01$ recently measured by EXAFS.[23]

B. Model II

An analysis of the experimental A_s value similar to that of the preceding section, but using Eq. (6) instead of Eq. (5), has also been carried for Mn^{2+}-doped fluoroperovskites. The results are also collected in Table I.

It must be pointed out that the value of the c constant derived from the experimental A_s values corresponding to $KMnF_3$ and $RbMnF_3$ is now $c=1.593\pm0.017$ instead of $c=1.269\pm0.017$, which is larger than that given by the calculations by Emery *et al.*[17] for $[MnF_6]^{4-}$ and also by all the calculations on $[NiF_6]^{4-}$ which give c near 1.3.[19–21]

By inspecting Table I we see that model I predicts more drastic ligand relaxation effects than model II. In the cases of $KZnF_3$:Mn^{2+} and $RbCdF_3$:Mn^{2+} the values derived by model I appear to be in better agreement with EXAFS results than those derived by model II. Nevertheless, the uncertainties involved in the R values (Table I) prevent us from a definite conclusion about this point. Additional EXAFS measurements on systems such as $CsCaF_3$:Mn^{2+}, where the difference between the R values calculated by models I and II are beyond the involved errors, would clarify the present situation.

Hence, owing to the present arguments and especially to the fact that the value of c constant calculated through model I is closer to the theoretical results on $[MnF_6]^{4-}$ and $[NiF_6]^{4-}$ than that obtained through model II, we shall only apply model I in the analysis of the experimental A_s values discussed in the next sections.

C. Thermal-expansion effects on A_s

It is clear that if A_s is sensitive to changes in R, A_s should reflect the variations undergone by the $[MnF_6]^{4-}$ cluster due to thermal-expansion effects. In particular, it should be possible to derive the thermal-expansion coefficient α for $[MnF_6]^{4-}$ in a given lattice by inspecting the variations on A_s due to temperature changes.

In connection with this, Jeck and Krebs[33] observed, for $KZnF_3$:Mn^{2+}, that A_s goes from $17.4\pm0.2\times10^{-4}$ cm^{-1} at room temperature to $18.10\pm0.01\times10^{-4}$ cm^{-1} at 4.2 K. If we apply Eq. (5) of model I taking $c=1.269$ to this situation, it is found that R (4.2 K)$=2.0717\pm0.0002$ Å, while the R value at room temperature is 2.082 ± 0.003 Å. From these values it is found that $\alpha=(17.2\pm5.4)\times10^{-6}$ K^{-1}, which compares very well with $\alpha=16.52\times10^{-6}$ K^{-1} reported for $RbMnF_3$ at 300 K through neutron-diffraction measurements.[25]

It is worth noting here that this agreement may be somewhat fortuitous because the α values for $[MnF_6]^{4-}$ in $RbMnF_3$ and in $KZnF_3$:Mn^{2+} must not be necessarily the same, but they could be very similar.

Another system in which the variations of A_s with the temperature has been investigated is $KMgF_3$:Mn^{2+}. In this case, analyzing the experimental A_s values reported by Dormann *et al.*[25] in the range 355—1300 K by means of model I, it is found that the mean thermal-expansion coefficient $\alpha=(23\pm11)\times10^{-6}$ K^{-1}. This value is again comparable to the mean value $\alpha=(20.63\pm0.13)\times10^{-6}$ K^{-1} for $RbMnF_3$ measured in the same range of temperatures.[34]

IV. Mn^{2+} IN SLIGHTLY DISTORTED O_h SYSTEMS

In this section we analyze the experimental A_s values of systems in which there are two inequivalent Mn—F bonds characterized by two different Mn—F distances. When Mn^{2+} enters a lattice (such as ZnF_2 or K_2ZnF_4) replacing a C^{2+} cation, this is related to the appearence of two inequivalent C^{2+}—F^- distances in the host lattice. These two distances of the host lattice will be denoted as R_0(I) and R_0(II), where R_0(I) corresponds to the shortest bond. Once Mn^{2+} replaces C^{2+} those distances are converted into R(I) and R(II), characteristic of the distorted $[MnF_6]^{4-}$ cluster.

In this analysis we shall assume that model I is also valid for those systems in which the $[MnF_6]^{4-}$ cluster is slightly distorted from O_h symmetry. From the experimental shf A_s(I) and A_s(II) constants we can derive two values—λ_s(I) and λ_s(II)—by means of Eq. (5); λ_s(I) is thus the $2s$ (F^-) admixture coefficient in the $3d$ (e_g) orbital for an octahedral situation in which the Mn—F distance is $R=R$(I) for every Mn—F bond. Therefore, we shall assume that the connection between λ_s(I) and λ_s(II) with the corresponding group-overlap integrals denoted as S_s(I) and S_s(II) is simply given by

$$\lambda_s(\text{I})=cS_s(\text{I}),\quad \lambda_s(\text{II})=cS_s(\text{II}), \tag{7}$$

where $c=1.269\pm0.017$ after the results obtained for Mn^{2+}-doped fluoroperovskites using model I. Thus, assuming Eq. (7) is correct, we are now able to predict the values of R(I) and R(II) from the experimental A_s(I) and A_s(II) values for each system involving a distorted $[MnF_6]^{4-}$ cluster.

The first of these systems analyzed are MnF_2 and ZnF_2:Mn^{2+}. In the former case R(I) and R(II) are known from x-ray-diffraction measurements by Baur,[35] while the

TABLE II. Values of R(I) and R(II) derived assuming Eq. (7) is correct from the experimental A_s(I) and A_s(II) values for slightly distorted O_h systems. Note that in the case of K_2ZnF_4 and K_2MgF_4 the short bond appears to become the long bond when Mn^{2+} replaces the divalent cation. See, however, the paper by G. Lehmann quoted in Ref. 1 and the paper by Rousseau *et al.* (Ref. 9).

Lattice	R_0(I) (Å)	R_0(II) (Å)	A_s(I) (experiment) (10^{-4} cm^{-1})	A_s(II) (experiment) (10^{-4} cm^{-1})	Ref.	R(I) (Å)	R(II) (Å)
MnF_2	2.102	2.132	16.2 ±0.3	15.4 ±0.3	36,37	2.101±0.013	2.115±0.013
ZnF_2:Mn^{2+}	2.015	2.043	16.57±0.19	15.11±0.16	5	2.095±0.010	2.120±0.010
K_2MnF_4	2.086		17.5 ±0.3	14.8 ±0.3	10	2.081±0.012	2.126±0.012
K_2ZnF_4:Mn^{2+}	1.966	2.0045	14.9 ±0.4	18.1 ±0.2	38	2.124±0.015	2.072±0.010
K_2MgF_4:Mn^{2+}	1.985	1.991	13.7 ±0.4	18.9 ±0.3	39	2.146±0.015	2.060±0.012

values of A_s(I) and A_s(II), given in Table II for MnF_2, are those derived by Keffer *et al.*[36] from the NMR data of Shulman and Jaccarino.[37] It should be recalled here that the derivation of A_s(I) and A_s(II) by Keffer *et al.*[36] involves some approximation. Owing to this fact, the EPR values[5] A_s(I) and A_s(II) obtained for ZnF_2:Mn^{2+} are more accurate than those derived for MnF_2. Moreover, the values of R(I) and R(II) derived in the present work using the data by Keffer *et al.*,[36] are very close to the crystallographic data by Baur.[35] In particular, there is good agreement with Baur's data in the case of R(I), while the predicted value of R(II) is slightly smaller. This slight discrepancy is, however, not significant in view of the approximations involved for deriving A_s(I) and A_s(II) and which are discussed by Keffer *et al.*[36] and also by Marshall and Stuart.[7]

The analysis of the more accurate data for ZnF_2:Mn^{2+} reveals that when Mn^{2+} enters the ZnF_2 lattice substitutionally, the Mn—F distances are practically equal to those of MnF_2 which is isomorphous to ZnF_2. This fact was already suggested by Clogston *et al.*[5] in their interpretation of the experimental data on MnF_2 and ZnF_2:Mn^{2+}.

The next system which has been studied is K_2MnF_4, where only $R(I)=2.086$ Å is known from x-ray-diffraction measurements. It can be seen from Table II that the present method predicts $R(I)=2.081\pm0.012$ Å, which is in good agreement with the true value. Furthermore, the experimental A_s(II) value leads us to predict $R(II)=2.126\pm0.012$ Å, which is a bit larger than $R(II)=2.11$ Å or $R(II)=2.10$ Å suggested by Bucci *et al.*[10] and Rousseau *et al.*,[9] respectively.

The results of Table II show that when Mn^{2+} enters K_2ZnF_4 or K_2MgF_4 the distances R(I) and R(II) of the distorted octahedron are similar to those for K_2MnF_4, $|R(I)-R(II)|$ being around 0.05 Å. This behavior is similar to that found when comparing Mn^{2+}:ZnF_2 and MnF_2, though in this case the difference between R(I) and R(II) is smaller.

V. Mn^{2+} IN ALKALI FLUORIDES

Since the early work by Watkins,[40] it is known that in quenched samples of Mn^{2+}-doped alkali halides, several Mn^{2+} centers can be formed. In these centers, Mn^{2+}, which is always surrounded by six nearest-neighbor halide anions, is usually associated to a cation vacancy which can be located in different places of the lattice. The position of the vacancy affects mainly the zero-field splitting term of the spin Hamiltonian, but not the corresponding shf tensor. In this way, the difference between the A_s values for spectra III_2 and III_4 (in Watkins's notation) in RbF:Mn^{2+} is within the experimental error.[41]

Moreover, in order to be consistent we analyze in this section the experimental A_s values at room temperature for III_4 spectra of Mn^{2+}-doped NaF, KF, and RbF. As the EPR results indicate that the six F^- ligands are equivalent in practice, here we shall use model I for a perfect O_h symmetry as applied in Sec. III. The results of Table III indicate that in spite of the great value of R_0 for RbF and KF compared to $R_0(Mn-F)=2.13$ Å, significant inward relaxation processes occur when Mn^{2+} enters

TABLE III. Values of R derived from experimental values of A_s measured at room temperature, using model I, for Mn^{2+} in alkali fluorides.

Lattice	R_0 (Å)	$A_s(10^{-4}\ cm^{-1})$ (experiment)	Reference	R (Å)	$\Delta R/R_0$ (%)
$RbF:Mn^{2+}$	2.815	11.5 ± 0.4	41	2.192 ± 0.016	22.1
$KF:Mn^{2+}$	2.674	12.3 ± 0.5	41	2.174 ± 0.019	18.7
$NaF:Mn^{2+}$	2.317	13.3 ± 0.3	42	2.154 ± 0.013	7.0

these lattices substitutionally. In this way the calculated values of $\Delta R/R_0$ ($\Delta R = R_0 - R$) for $RbF:Mn^{2+}$ and $KF:Mn^{2+}$ are 22.1% and 18.7%, respectively. It is worth noting here that $\Delta R/R_0$ values up to 27% have been estimated for Ag^0- and Cu^0-doped alkali halides.[2]

Finally, Table II tell us that the R values for Mn^{2+}-doped NaF, KF, and RbF are once more ordered in the same way as the corresponding R_0 values. This feature, also found in the case of Mn^{2+}-doped fluoroperovskites, has been recently pointed out for Cu^0 and Ag^0 in alkali-chloride lattices.[2]

VI. DISCUSSION

The present method, in which no empirical parameters are involved, has been shown to predict satisfactorily the Mn—F distances for $KZnF_3:Mn^{2+}$ and $RbCdF_3:Mn^{2+}$ recently measured by means of the EXAFS technique.

However, it turns out that model I which neglects the influence of the $1s$ (F^-) orbital upon A_s gives better results than model II in which that influence is considered. This conclusion is in agreement with the previous work by Hall *et al.*[8] In particular, the value of the c constant for model II seems to be too large when compared to theoretical predictions. This fact perhaps indicates that the MO approximation given by Eq. (1) for describing the one-electron wave functions is essentially right in the middle region between Mn^{2+} and F^-, but not in the core regions of Mn^{2+} and F^-. In other words, the $|d(e_g)\rangle$ function does not penetrate into the core region of F^- ions. If that is so, the orthogonalization requirement of the valence $|e_g^*\rangle$ orbital of $[MnF_6]^{4-}$ to the core $1s$ levels of F^- ions would be automatically fulfilled because of the orthogonality between the $1s$ (F^-) and $2s$ (F^-) orbitals. Moreover, further research about this point is desirable. In particular, further EXAFS measurements on systems such as $CsCaF_3:Mn^{2+}$, for which the R values predicted by models I and II are rather different, could help to clarify this point.

The main assumption involved through the present work is just that the relation between $\lambda_s(R)$ and $S_s(R)$ is a constant c independent of R. However, the theoretical calculations by Emery *et al.*[17] outline that the value of this "constant" c changes around 8% when R goes from 1.9 to 2.3 Å. As the results obtained in the present work indicate that the R values for $[MnF_6]^{4-}$ in several lattices go only from 2.06 to 2.20 Å, our assumption turns out to be strongly consistent.

The results of Sec. IV point out that the present method for deriving the Mn—F distances from the corresponding isotropic shf constants is also useful for systems whose symmetry is slightly distorted from O_h and thus exhibit two inequivalent Mn—F bonds. In these systems, however, there could appear, in principle, a $4s$ (Mn^{2+}) admixture in Eq. (1) which would modify the theoretical framework.[9] The results of the present work suggest that such admixture is negligible. This fact can be related to the recent *DV-Xα* calculations on $KMnF_3$ and MnF_2, which indicate that the role of $4s$ and $4p$ orbitals of Mn^{2+} in the bond of these compounds is nearly negligible.[16]

As the Mn—F bond is mainly ionic, the results derived in Secs. III and V for systems involving the octahedral O_h cluster can be understood in terms of a competition between (1) the tendency of the substitutional Mn^{2+} ions to form Mn—F bonds having the "natural" distance $R_0(\text{Mn—F}) = 2.13$ Å equal to the sum of ionic radii of Mn^{2+} and F^-, and (2) the tendency of the host lattice to avoid such ligand relaxation.

Owing to this, the host lattices with the largest differences between R_0 and R_0(Mn—F) would give rise, in principle, to the largest differences between the corresponding R values and R_0(Mn—F) as it is observed. Moreover, the present results clearly show that the first tendency dominates and thus significant ligand relaxation effects can happen. In this sense, for instance, the results on $RbF:Mn^{2+}$ indicate that the anion-cation distance changes from $R_0 = 2.82$ Å for the perfect lattice to $R = 2.19$ Å, giving rise to a $\Delta R/R$ value of about 22%.

It is now worth noting here that in the relation of Model I between A_s and λ_s we have assumed $N = 1$. Though the Mn—F bond is highly ionic, this assumption is not rigorously true. In fact, if we take into account that $\langle e_g^* | e_g^* \rangle = 1$ and take $f_\sigma = 1.1\%$, $f_s = 0.5\%$, $S_{p\sigma} = 0.1222$, and $S_s = 0.1015$ (for $R = 2.095$ Å), we find $N = 1.009$. This value of N would give rise to changes in the calculated values of λ_s and c less than 1%.

Some of the previous empirical relations proposed between A_s and R are simply linear relations of the form

$$\Delta A_s/\Delta R = -K \ , \tag{8}$$

where K is a constant whose value is $K = (1.1 \pm 0.3) \times 10^{-2}\ cm^{-1}\,Å^{-1}$ following Bucci *et al.*,[10] while Shulman and Knox[6] give $K = 5.65 \times 10^{-2}\ cm^{-1}\,Å^{-1}$.

Although model I of the present work predicts that A_s varies, in fact, as $S_s^2(R)$, it is clear that a linear relation between A_s and R can be compatible with a more general relation provided the region of R values for which the linear relation is also valid is small enough.

In particular, Fig. 1 indicates that for Mn^{2+}-doped

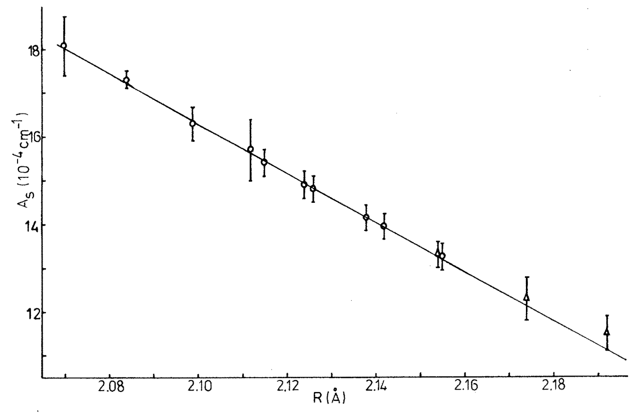

FIG. 1. Plot of the experimental A_s values for Mn^{2+}-doped fluoroperovskites (○) and alkali fluorides (△) vs the corresponding value of R derived in the present work by means of model I.

fluoroperovskites, Eq. (8) is well verified, K being equal to 0.57×10^{-2} cm^{-1} Å^{-1}. In this case of course, K should be interpreted as

$$K=-\frac{c^2}{15}A^0_{2s}\left[\frac{dS_s^2(R)}{dR}\right]_{R=R_0(\mathrm{Mn-F})}, \tag{9}$$

following the results of the present work.

If we apply this approximate linear relation for measuring R for Mn^{2+}-doped RbF we find a difference of only 0.007 Å, with respect to the value obtained by means of Eqs. (4) and (5).

The value of this constant K tells us that if we are capable of measuring A_s with an accuracy of 0.01 G such as it is achieved in ENDOR experiments, then we could detect, by means of the variations of A_s, changes in R down to about 2.10^{-4} Å produced by external hydrostatic pressures, thermal-expansion effects, etc. In this way, for instance, if we assume a thermal-expansion coefficient α to be about 10^{-5} K^{-1}, we could observe changes in R produced by thermal-expansion effects when the temperature varies only around 10 K.

In conclusion, Eq. (4) of the present work, which is not empirical but well founded in MO calculations on $[MnF_6]^{4-}$, appears to be suitable for obtaining satisfactory information on R for $[MnF_6]^{4-}$ embedded in different fluoride lattices using the data derived from EPR or ENDOR spectroscopy.

In this sense the experimental value of A_s can be regarded as a kind of probe which provides us with a direct information about the R value. As mentioned in the Introduction this idea is not true in the case of the anisotropic shf constant whose variation with R is much more complicated to predict.

The present technique could also be very useful for deriving the R value of $[MnF_6]^{4-}$ in different liquid solutions provided the shf structure be resolved. Moreover, in this case, if the motional-narrowing regime is established, the A_s value is measured directly because the anisotropic shf tensor averages zero. Though we do not know data on $[MnF_6]^{4-}$ in liquid solutions, however, Levanon *et al.*[43] observed shf structure for $[FeF_6]^{3-}$ in water.

With regard to the applicability of the present techniques to complexes other than $[MnF_6]^{4-}$, we shall briefly mention two main points of the problem.

(1) If the complexes are nearly ionic then a similar development to that performed here could be reasonable. In these cases the main problem would be the knowledge of the c constant provided the approximate assumption involved in Eq. (4) is reliable.

In this sense, for instance, recent *ab initio* calculations for $[CrF_6]^{5-}$ and $[CrF_6]^{4-}$ clusters[44] reveal that for the former λ_s/S_s undergoes a variation of only 5% when R goes from 1.7 to 2.3 Å, the value of the c constant being 1.07. In the case of $[CrF_6]^{4-}$, however, λ_s/S_s experiences an increase of 12% when R increases from 1.7 to 2.3 Å, the mean value of the c constant being 1.14.

(2) If the complex is moderately or strongly covalent the present framework is not suitable for determining R from A_s.

We are currently working along this line. The results of such a work are planned to be published in the near future.

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