

# Dependence of the optical spectrum of $\text{MnF}_6^{4-}$ on the $\text{Mn}^{2+}\text{-F}^-$ distance

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We have measured by means of photoluminescence the energy of crystal-field peaks for  $\text{RbCdF}_3\text{:Mn}^{2+}$  and  $\text{KZnF}_3\text{:Mn}^{2+}$  where the value of the  $\text{Mn}^{2+}\text{-F}^-$  distance,  $R$ , derived by EXAFS is  $R = 2.13 \pm 0.01 \text{ \AA}$  and  $R = 2.08 \pm 0.01 \text{ \AA}$ , respectively. From these data and those for  $\text{RbMnF}_3$  and  $\text{KMnF}_3$  we have studied the dependence on  $R$  of the  $B$ ,  $C$ , and  $10 Dq$  parameters for the  $\text{MnF}_6^{4-}$  complex. This analysis reveals that within the experimental errors,  $B$  and  $C$  are constant in the range  $2.07 < R < 2.14 \text{ \AA}$ , in agreement with recent self-consistent calculations for  $\text{MnF}_6^{4-}$ , which also predict that  $10 Dq = KR^{-n}$ , where  $K$  and  $n$  are constant. The present study confirms this dependence,  $n$  being 4.4 which is also in accord to the theoretical predictions. The best values of  $R$  derived from optical spectra are found to be  $R = 2.141 \pm 0.004 \text{ \AA}$  (for  $\text{RbCdF}_3\text{:Mn}^{2+}$ ) and  $R = 2.075 \pm 0.004 \text{ \AA}$  (for  $\text{KZnF}_3\text{:Mn}^{2+}$ ). The present analysis also points out that by measuring the changes induced on the optical spectrum of  $\text{MnF}_6^{4-}$  in a given lattice we can detect changes in the  $\text{Mn}^{2+}\text{-F}^-$  distance down to  $10^{-3} \text{ \AA}$ . In this way we have derived the difference,  $\Delta R$ , between  $R$  at room temperature and at 77 K for  $\text{KZnF}_3\text{:Mn}^{2+}$ . The obtained value  $\Delta R = (9 \pm 1) 10^{-3} \text{ \AA}$  is in agreement with the one  $\Delta R = (10 \pm 3.5) 10^{-3} \text{ \AA}$  derived previously from the variations undergone by the isotropic superhyperfine constant  $A_s$ . Finally the present results are compared to those for some complexes of  $\text{Eu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cr}^{3+}$ .

## I. INTRODUCTION

Crystal-field transitions for ionic compounds containing transition-metal cations can be understood in terms of the  $\text{MX}_n$  complex formed by the metal cation  $M$  and the  $n$  nearest anions  $X$ .

The true distance  $R$  between  $M$  and  $X$  depends, however, on the lattice where the complex is placed. This fact induces differences in the optical and magnetic response due to a given complex but located in different lattices.

In spite of this, little theoretical and experimental work has been devoted to establishing quantitatively the dependence of crystal-field spectra of transition-metal complexes upon  $R$ . Efforts in this direction can, however, be useful in determining from optical measurements the changes in  $R$  induced by applied hydrostatic pressures, thermal expansion effects, etc. In this paper we present a study of the dependence of the crystal-field spectrum of  $\text{MnF}_6^{4-}$  upon  $R$ . This complex comes from  $\text{Mn}^{2+}$  whose configuration is  $3d^5$ . The present study has been helped by the following circumstances: (1) The advent of the first Hartree-Fock-Roothaan calculation on crystal-field transitions for the  $\text{MnF}_6^{4-}$  complex (*in vacuo*) performed for several values of  $R$ .<sup>1</sup>

Also for  $\text{MnF}_6^{4-}$  in the  $\text{RbMnF}_3$  lattice the effect of the electrostatic potential of the "rest of the lattice" upon crystal-field transitions has been calculated<sup>1</sup> showing that it is negligible. A survey of these results is given in a later section. (2) The EXAFS measurements<sup>2</sup> carried out on two cubic fluoroperovskite lattices (at room temperature) doped with  $\text{Mn}^{2+}$ . From them  $R$  has been derived to be

$$R = 2.13 \pm 0.01 \text{ \AA} \text{ for } \text{RbCdF}_3\text{:Mn}^{2+}$$

and

$$R = 2.08 \pm 0.01 \text{ \AA} \text{ for } \text{KZnF}_3\text{:Mn}^{2+}.$$

Also these figures are quite consistent with those derived from the experimental isotropic superhyperfine constant  $A_s$  at room temperature (RT) for both systems.<sup>3</sup>

By virtue of these facts we have analyzed the crystal-field spectra for  $\text{MnF}_6^{4-}$  in cubic fluoroperovskite lattices where the  $\text{Mn}^{2+}\text{-F}^-$  distance is reasonably well known. Thus, besides the spectra of  $\text{RbMnF}_3$ <sup>4,5</sup> and  $\text{KMnF}_3$ ,<sup>5</sup> we have studied those for  $\text{RbCdF}_3\text{:Mn}^{2+}$  and  $\text{KZnF}_3\text{:Mn}^{2+}$ .

To our knowledge no crystal-field transitions have been reported for  $\text{RbCdF}_3\text{:Mn}^{2+}$ , while only a partial account of them has been given for  $\text{KZnF}_3\text{:Mn}^{2+}$ .<sup>6,7</sup> Owing to this, we have measured the crystal-field transitions for  $\text{RbCdF}_3\text{:Mn}^{2+}$  and  $\text{KZnF}_3\text{:Mn}^{2+}$  by means of photoluminescence techniques.

Through the analysis of the experimental results for these four systems we have derived the dependence of  $B$ ,  $C$ , and  $10 Dq$  parameters on  $R$  in the range  $2.07 < R < 2.14 \text{ \AA}$ . For checking the relation found between  $10 Dq$  and  $R$  we have also measured the variations undergone by the energy of crystal-field peaks of  $\text{KZnF}_3\text{:Mn}^{2+}$  when sample is cooled from RT to 77 K.

The change in  $R$ , termed  $\Delta R$ , derived from it is compared with the value  $\Delta R = (10 \pm 3.5) 10^{-3} \text{ \AA}$  previously obtained from the experimental variations of  $A_s$ .<sup>3</sup>

## II. EXPERIMENTAL

Powders of  $\text{RbCdF}_3\text{:Mn}^{2+}$  and  $\text{KZnF}_3\text{:Mn}^{2+}$  were kindly supplied by Leblé and Rousseau. The samples were the same on which EXAFS experiments were previously carried out.<sup>2</sup> KBr pellets formed with these powders were observed at RT through a Jobin-Ivon JY3D spectrofluorimeter. Excitation spectra for  $\text{RbCdF}_3\text{:Mn}^{2+}$  and  $\text{KZnF}_3\text{:Mn}^{2+}$  were recorded at 600 and 633 nm, respectively, using

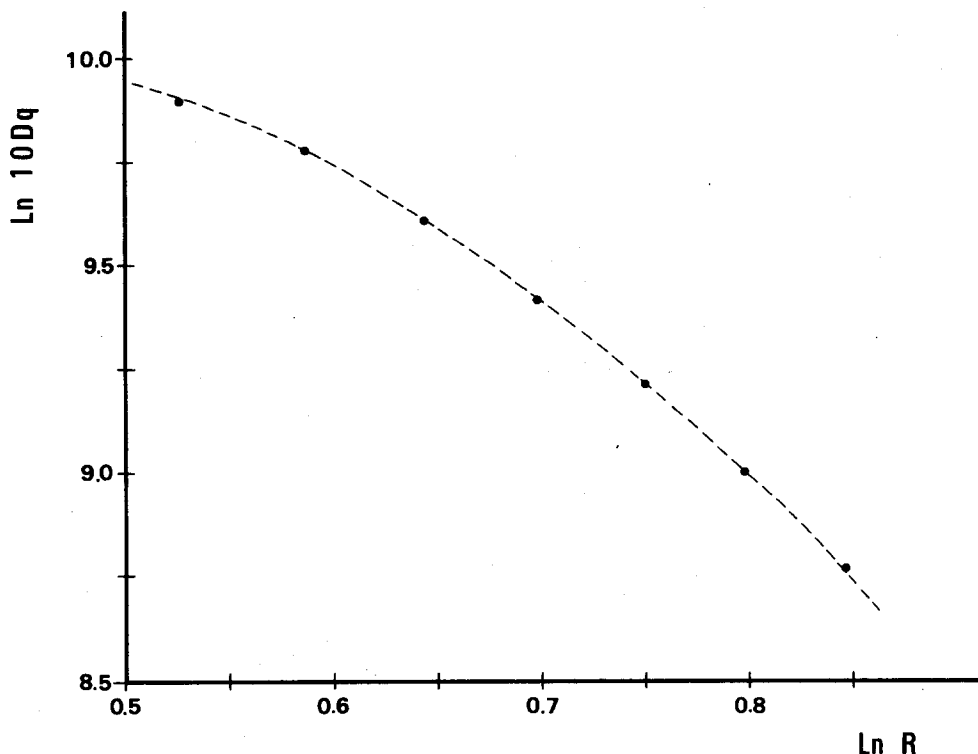


FIG. 1. Plot of the  $L$  10 Dq value derived from the theoretical calculation by Florez *et al.* (Ref. 1) vs  $LR$  in the range  $1.70 < R < 2.35 \text{ \AA}$ .

Oriel and Schott narrow band interference filters.

### III. THEORETICAL PREDICTIONS: A SURVEY

The main theoretical predictions by Florez *et al.*<sup>1</sup> on the dependence of the crystal-field spectrum of  $\text{MnF}_6^{4-}$  complex (*in vacuo*) due to changes of the  $\text{Mn}^{2+}-\text{F}^-$  distance  $R$  in the range  $1.70 < R < 2.30 \text{ \AA}$  are the following:

(1) The energy of the  ${}^4E(G)$ ,  ${}^4A_1(G)$  state [referred to the ground state  ${}^6A_1(S)$ ] is practically independent of  $R$ , lying at  $25\,700 \text{ cm}^{-1}$ .

(2) The same happens for the  ${}^4E(D)$  state, its energy being  $31\,000 \text{ cm}^{-1}$ .

(3) The remaining states arising from the  ${}^4G$ ,  ${}^4D$ , and  ${}^4P$  states of free  $\text{Mn}^{2+}$  all vary when  $R$  is changed, the most sensitive of them being the first excited state  ${}^4T_1(G)$ . Aside from this state also the  ${}^4T_2(G)$  and, to a minor extent, the  ${}^4T_2(D)$  have a smaller energy when  $R$  decreases. By contrast the energy of the  ${}^4T_1(P)$  increases slightly upon decreasing  $R$ .

In order to quantify the last conclusions we can fit the first principles energies derived for  $\text{MnF}_6^{4-}$  to the usual semiempirical expressions involving three parameters: the cubic field splitting  $10 Dq$  and the effective Racah parameters  $B$  and  $C$ . In this fitting Tree's ( $\alpha$ ) and seniority ( $\beta$ ) parameters are considered<sup>8</sup> and taken equal to  $\alpha = 65 \text{ cm}^{-1}$ ,  $\beta = -131 \text{ cm}^{-1}$ . That procedure is followed for every fitting throughout this paper. We have verified that fitting of theoretical results to crystal-field expressions involving  $B$ ,  $C$ , and  $10 Dq$  is reasonably good. As a measure of the fitting quality we use the rms deviation  $\sigma$  defined by

$$\sigma = \left[ \frac{1}{N-P} \sum_i (E_i^F - E_i^P)^2 \right]^{1/2},$$

where  $E_i^P$  and  $E_i^F$  correspond to input energies and to those

derived by fitting, respectively;  $P$  is the number of free parameters and  $N$  the number of data.  $E_i^F$  have been derived by searching to minimize

$$\sum_i \left[ \frac{E_i^F - E_i^P}{E_i^P} \right]^2.$$

We have found that in the range  $1.90 \text{ \AA} < R < 2.30 \text{ \AA}$   $\sigma$  is always less than  $360 \text{ cm}^{-1}$ .

When only the theoretical energy of the first six excited states with  $S = 3/2$  is considered in the fitting it is found that the effective  $B$  and  $C$  parameters are predicted to be essentially independent of  $R$ <sup>9</sup> and equal to the following values:  $B = 880 \text{ cm}^{-1}$ ;  $C = 3100 \text{ cm}^{-1}$ .

By contrast  $10 Dq$  strongly depends on  $R$  in the way depicted in Fig. 1. It can be seen in it that a dependence of  $10 Dq$  with  $R$  of the form

$$10 Dq = KR^{-n}, \quad (1)$$

where both  $K$  and  $n$  are constants is not rigorously true in the complete range of  $R$  values. Nevertheless Eq. (1) represents quite well the theoretical results in Fig. 1, in the neighborhood of a given value  $R$ , or, more precisely when  $R$  varies between  $R - \delta R$  and  $R + \delta R$ ,  $\delta R$  being equal to  $0.1 \text{ \AA}$ . The full range  $2\delta R = 0.20 \text{ \AA}$  is larger than that corresponding to the  $R$  values found for  $\text{Mn}^{2+}$  in cubic fluoropervskites and alkali fluorides by means of the analysis of the experimental  $A_1$  values.<sup>3</sup> From Fig. 1 and for  $R = 2.12 \text{ \AA}$  a value of the exponent  $n$  equal to 4.3 and a value  $10 Dq = 10\,200 \text{ cm}^{-1}$  can be derived.

The value of the exponent is a little higher than that calculated by Adachi *et al.*,<sup>10</sup>  $n = 3.4$  using the discrete variational  $X\alpha$  method. As regards  $10 Dq$  it is about  $2000 \text{ cm}^{-1}$  higher than that determined for  $\text{RbMnF}_3$ . This discrepancy in the calculations by Florez *et al.*<sup>1</sup> on the  $\text{MnF}_6^{4-}$  complex

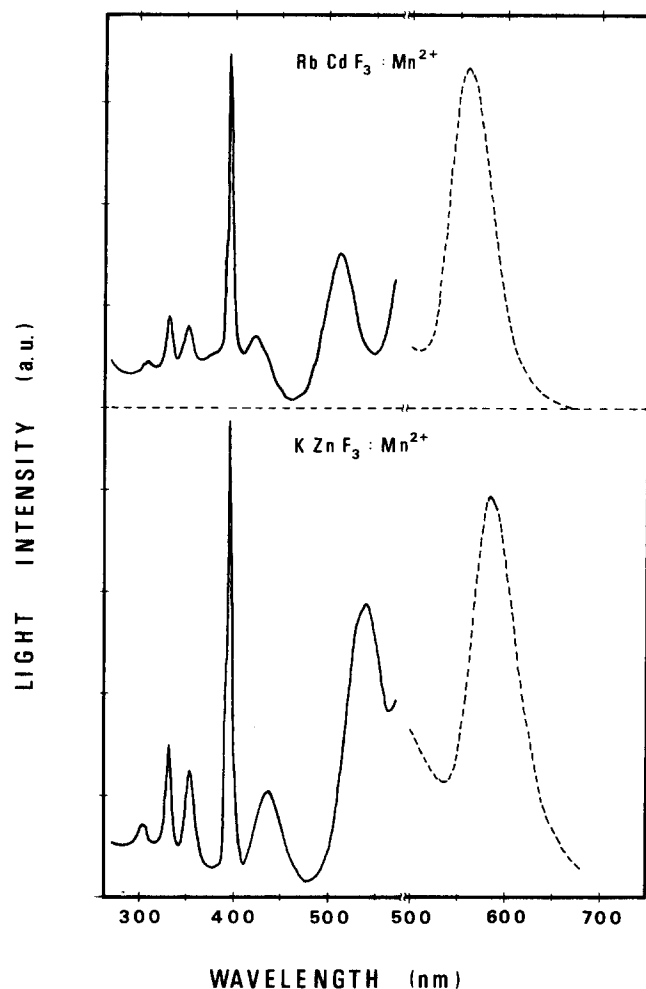


FIG. 2. Excitation (solid line) and emission (dotted line) spectra for  $\text{RbCdF}_3:\text{Mn}^{2+}$  and  $\text{KZnF}_3:\text{Mn}^{2+}$  measured at RT. No other crystal-field peaks were detected in the excitation spectra for the wavelength smaller than 280 nm.

*in vacuo* with respect to the experimental value in  $\text{RbMnF}_3$  is not alleviated by the introduction in the calculation of the electrostatic potential due to the "rest of the  $\text{RbMnF}_3$  lattice" upon the  $\text{MnF}_6^{4-}$  complex: the position of the excited quartet states is essentially the same as that for  $\text{MnF}_6^{4-}$  *in vacuo*.

The origin of this which supports the idea of complex as good for understanding the properties due to a transition cation in ionic lattices, was first pointed out by Sugano and Shulman.<sup>11</sup>

Anyway, the above theoretical result strongly suggests that cubic fluorperovskites are good lattices for studying experimentally the variations undergone by the optical spectrum of the  $\text{MnF}_6^{4-}$  cluster due to changes in the  $\text{Mn}^{2+}-\text{F}^-$  distance.

Finally, it is worth noting in Fig. 1 that for  $R = 2.33 \text{ \AA}$ , when 10 Dq is equal to  $8000 \text{ cm}^{-1}$   $n$  becomes 4.8. This value is still closer to the value  $n = 5$  obtained in crystal-field theory.

Nevertheless, this should be regarded only as a fortuitous coincidence. In fact crystal-field theory predicts for the  $\text{MnF}_6^{4-}$  cluster and for  $R = 2.12 \text{ \AA}$  a value 10 Dq = 1600

$\text{cm}^{-1}$  derived using  $\langle r^4 \rangle_{3d} = 4.5 \text{ a.u.}$  corresponding to free  $\text{Mn}^{2+}$  ion.<sup>12</sup>

It is worth noting here that the trends predicted by the theoretical calculation for the variation of the optical spectrum of  $\text{MnF}_6^{4-}$  with  $R$  are in fact those derived from the well-known Tanabe-Sugano diagrams but *assuming* that the effective parameters  $B$  and  $C$  are independent of  $R$ .<sup>13</sup> For  $\text{MnF}_6^{4-}$  however this assumption is *proved* to be essentially correct within the superior framework provided by the Hartree-Fock-Roothaan methodology.

#### IV. EXPERIMENTAL RESULTS: ANALYSIS

In Fig. 2 are reported the RT excitation and emission spectra corresponding to  $\text{RbCdF}_3:\text{Mn}^{2+}$  and  $\text{KZnF}_3:\text{Mn}^{2+}$ . As regards the excitation spectra, the most remarkable difference between them lies in the position of the  ${}^4T_1(G)$  peak: it lies at 512 nm for  $\text{RbCdF}_3:\text{Mn}^{2+}$  while it is placed at 539.5 nm for  $\text{KZnF}_3:\text{Mn}^{2+}$ .

In the same way the emission peak associated with the  ${}^4T_1(G) \rightarrow {}^6A_1(S)$  transition has a higher wavelength for  $\text{KZnF}_3:\text{Mn}^{2+}$  (582 nm) than for  $\text{RbCdF}_3:\text{Mn}^{2+}$  (560 nm). In Table I are reported the experimental energies of crystal-field peaks for  $\text{RbCdF}_3:\text{Mn}^{2+}$  and  $\text{KZnF}_3:\text{Mn}^{2+}$ . In this table are also included the corresponding positions for  $\text{RbMnF}_3$  and  $\text{KMnF}_3$  at RT taken from Refs. 4 and 5. It can be seen that the energy of the  ${}^4A_1(G)$ ,  ${}^4E(G)$  peak is practically the same for all systems, having a mean value of  $25\,240 \text{ cm}^{-1}$  which is only  $500 \text{ cm}^{-1}$  smaller than that calculated by Florez *et al.*<sup>1</sup> Also the  ${}^4E(D)$  peak energy is found to be nearly independent of the system, lying at  $30\,100 \text{ cm}^{-1}$ , a value which is  $\sim 1000 \text{ cm}^{-1}$  smaller than that predicted in the theoretical calculations.<sup>1</sup>

As regards the other transitions they depend on  $R$  following qualitatively the theoretical predictions discussed in the preceding section. In this sense the first  ${}^4T_1(G)$  peak is in fact the most sensitive to changes in  $R$  among the six crystal-field peaks experimentally observed.

The values of the  $B$ ,  $C$ , and 10 Dq parameters obtained from the fitting of the experimental peak energies for the four systems considered are also included in Table I. It can be seen that  $B$  and  $C$  are in fact the same for the four systems within the experimental error and lie close to the values  $B = 880 \text{ cm}^{-1}$ ;  $C = 3100 \text{ cm}^{-1}$  derived from the theoretical calculations by Florez *et al.*<sup>1</sup> However 10 Dq experiences significant variations going from  $7150 \text{ cm}^{-1}$  for  $\text{RbCdF}_3:\text{Mn}^{2+}$  to  $8220 \text{ cm}^{-1}$  for  $\text{KZnF}_3:\text{Mn}^{2+}$ . In Fig. 3 is shown a plot of the experimental 10 Dq values vs the corresponding value of  $R$  derived from x-ray diffraction data or from EXAFS measurements (for  $\text{RbCdF}_3:\text{Mn}^{2+}$  and  $\text{KZnF}_3:\text{Mn}^{2+}$ ). That plot shows that the experimental results are consistent with a dependence of 10 Dq vs  $R$  given by Eq. (1). In order to obtain the most reasonable values for  $K$  and for the exponent  $n$  we have fitted the experimental results to an expression of this kind, searching a minimum value for the quantity

$$M = \sum_i p_i (Y_i^D - Y_i^F)^2,$$

where  $Y = L(10 \text{ Dq})$ ,  $Y_i^D$  correspond to the four experimen-

TABLE I. Experimental energies (in  $\text{cm}^{-1}$ ) of crystal-field peaks for  $\text{RbCdF}_3: \text{Mn}^{2+}$  and  $\text{KZnF}_3: \text{Mn}^{2+}$  (present work) and for  $\text{RbMnF}_3$  and  $\text{KMnF}_3$  (derived from Refs. 4 and 5) measured at room temperature.

Peak <sup>b</sup> energy	$\text{KZnF}_3: \text{Mn}^{2+}$ $R = 2.08 \pm 0.01 \text{ \AA}^a$		$\text{KMnF}_3$ $R = 2.095 \text{ \AA}^a$		$\text{RbMnF}_3$ $R = 2.120 \text{ \AA}^a$		$\text{RbCdF}_3: \text{Mn}^{2+}$ $R = 2.13 \pm 0.01 \text{ \AA}^a$	
	Experimental	Fitting	Experimental	Fitting	Experimental	Fitting	Experimental	Fitting
${}^4T_1(G)$	$18\,530 \pm 40$	18 568	18 900	18 957	19 300	19 347	$19\,530 \pm 40$	19 617
${}^4T_2(G)$	$22\,830 \pm 50$	22 878	23 120	23 131	23 310	23 355	$23\,670 \pm 50$	23 503
${}^4A_1, {}^4E(G)$	$25\,210 \pm 20$	25 210	25 245	25 245	25 275	25 275	$25\,230 \pm 20$	25 230
${}^4T_2(D)$	$28\,180 \pm 70$	28 323	28 200	28 424	28 250	28 486	$28\,350 \pm 70$	28 534
${}^4E(D)$	$30\,080 \pm 50$	30 110	30 150	30 138	30 150	30 119	$30\,070 \pm 50$	30 095
${}^4T_1(P)$	$32\,750 \pm 140$	33 108	32 550	32 917	32 360	32 742	$32\,270 \pm 140$	32 434
$B^d$	830		829		822		825	
$C^d$	3122		3131		3151		3136	
10 Dq <sup>d</sup>	8220		7855		7500		7150	
$\sigma^e$	226		250		263		180	

<sup>a</sup>The values of  $R$  derived from x-ray diffraction data or from EXAFS (for  $\text{RbCdF}_3: \text{Mn}^{2+}$  and  $\text{KZnF}_3: \text{Mn}^{2+}$ ).<sup>b</sup>The values of peak energies derived from fitting and the corresponding  $B$ ,  $C$ , and 10 Dq parameters (in  $\text{cm}^{-1}$ ).<sup>c</sup>The value of the rms deviation,  $\sigma$  (in  $\text{cm}^{-1}$ ).<sup>d</sup>The errors for  $B$ ,  $C$ , and 10 Dq are as follows: for  $B = \pm 7 \text{ cm}^{-1}$ ; for  $C = \pm 17 \text{ cm}^{-1}$ ; for 10 Dq =  $\pm 60 \text{ cm}^{-1}$ .

tal points and  $Y_i^F$  to the value obtained by fitting. The  $p_i$  factor takes into account the errors involved on 10 Dq and  $R$  for each system.

As the error on  $R$  for  $\text{RbCdF}_3: \text{Mn}^{2+}$  and  $\text{KZnF}_3: \text{Mn}^{2+}$  is  $\pm 0.01 \text{ \AA}$  we have taken  $p = 1$  for these systems and  $p = 10$  for  $\text{KMnF}_3$  and  $\text{RbMnF}_3$ .

It can be seen in Fig. 3 that the result of this fitting is good leading to a value of the exponent  $n = 4.45$  which is in good agreement with that derived from the theoretical calculations by Florez *et al.*<sup>1</sup> in the region  $2.0 < R < 2.30 \text{ \AA}$ . At the same time if 10 Dq is given in  $\text{cm}^{-1}$  and  $R$  in  $\text{\AA}$  then the value of  $K$  is found to be  $K = 2.113 \times 10^5$ .

The present results are thus quite consistent with the

values  $R = 2.08 \pm 0.01 \text{ \AA}$  and  $R = 2.13 \pm 0.01 \text{ \AA}$  recently derived from EXAFS for  $\text{KZnF}_3: \text{Mn}^{2+}$  and  $\text{RbCdF}_3: \text{Mn}^{2+}$ , respectively.<sup>2</sup> Furthermore if now we assume Eq. (1) and accept the present values of  $K$  and  $n$  we derive from the experimental 10 Dq values for  $\text{RbCdF}_3: \text{Mn}^{2+}$  and  $\text{KZnF}_3: \text{Mn}^{2+}$  the corresponding  $\text{Mn}^{2+}-\text{F}^-$  distances shown in Table II. It can be seen in it that the error in  $R$  ( $\pm 4 \times 10^{-3} \text{ \AA}$ ) involved in the present method, arising from that corresponding to 10 Dq, is smaller than that found for EXAFS measurements ( $\pm 10^{-2} \text{ \AA}$ ).

The present analysis then leads us to the conclusion that the optical spectrum of  $\text{MnF}_6^{4-}$  in ionic lattices conveys, in fact, useful information on the true value of the  $\text{Mn}^{2+}-\text{F}^-$

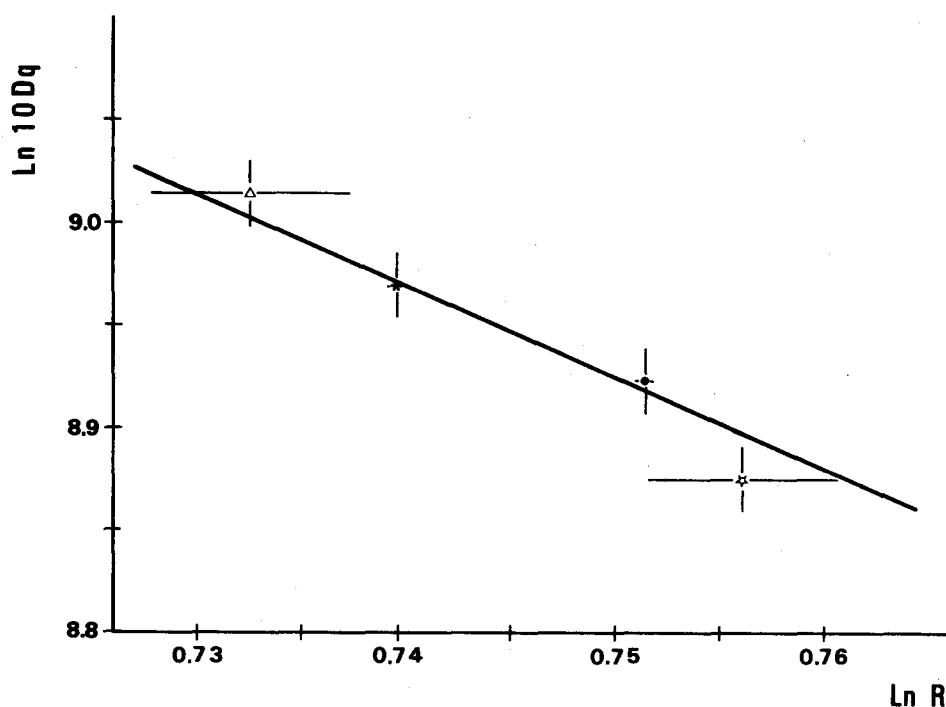


FIG. 3. Plot of the experimental values of  $L$  (10 Dq) vs  $LR$  for  $\text{RbCdF}_3: \text{Mn}^{2+}$  ( $\star$ ),  $\text{RbMnF}_3$  ( $\bullet$ ),  $\text{KMnF}_3$  ( $+$ ), and  $\text{KZnF}_3: \text{Mn}^{2+}$  ( $\triangle$ ) including the corresponding errors. The solid line corresponds to the fitting of experimental points to Eq. (1).

TABLE II. Values of the  $\text{Mn}^{2+}-\text{F}^-$  distance at room temperature for  $\text{RbCdF}_3: \text{Mn}^{2+}$  and  $\text{KZnF}_3: \text{Mn}^{2+}$  derived from EXAFS (Ref. 2), from the  $A_s$  value measured by EPR (Ref. 3), and from optical data (present work).

System	$R$ (Å) (EXAFS)	$R$ (Å) (EPR)	$R$ (Å) (OPTICAL)
$\text{RbCdF}_3: \text{Mn}^{2+}$	$2.13 \pm 0.01$	$2.124 \pm 0.012$	$2.141 \pm 0.004$
$\text{KZnF}_3: \text{Mn}^{2+}$	$2.08 \pm 0.01$	$2.084 \pm 0.012$	$2.075 \pm 0.004$

distance.

In particular, this technique can be useful for measuring the variations in  $R$  induced on a given sample by thermal expansion effects, applied hydrostatic pressures, etc. For this goal it suffices to follow the changes induced in the position of the  ${}^4T_1(G)$  peak provided the effective  $B$  and  $C$  parameters remain unchanged. Anyway this can be checked by looking at the position of the sharp  ${}^4E(G)$ ,  ${}^4A_1(G)$  peak. For a supplementary test of the validity of the present methodology we have derived the difference, termed  $\Delta R$ , between the  $R$  values for  $\text{KZnF}_3: \text{Mn}^{2+}$  corresponding at RT and at 77 K. We have verified that the position of the  ${}^4E(G)$ ,  ${}^4A_1(G)$  peak lies also at 396.7 nm at 77 K. By contrast we have noticed that the wavelength of the  ${}^4T_1(G)$  peak, lying at 539.5 nm at RT, experiences a shift of  $4.4 \pm 0.5$  nm at 77 K. This shift implies an increase in 10 Dq equal to  $155 \pm 17$   $\text{cm}^{-1}$ , which by virtue of Eq. (1) means that  $\Delta R = (9 \pm 1)10^{-3}$  Å. This value compares very well with that derived<sup>3</sup> from the variations undergone by  $A_s$ , which is equal to

$$\Delta R = (10 \pm 3.5)10^{-3} \text{ Å}.$$

## V. FINAL REMARKS

The main trends of the dependence of the optical spectrum of  $\text{MnF}_6^{4-}$  upon  $R$  derived from the theoretical calculations by Florez *et al.*<sup>1</sup> are supported by the present results. Also this study stresses the usefulness of optical measurements for gaining a good insight into the true value of the  $\text{Mn}^{2+}-\text{F}^-$  distance for  $\text{MnF}_6^{4-}$  in an ionic lattice.

In this way if we are able to detect changes in the peak energies for  $\text{MnF}_6^{4-}$  in a given lattice with an accuracy of at least,  $\pm 20$   $\text{cm}^{-1}$  then we can measure changes in the  $\text{Mn}^{2+}-\text{F}^-$  distance down to  $10^{-3}$  Å. This accuracy can hardly be achieved through EXAFS or EPR measurements.

In the later case<sup>3</sup> for getting an accuracy of  $10^{-3}$  Å on the  $\text{Mn}^{2+}-\text{F}^-$  distance we need to detect changes in the isotropic superhyperfine constant  $A_s$  of about  $0.06 \cdot 10^{-4}$   $\text{cm}^{-1}$ . However the experimental error in the  $A_s$  value measured by EPR<sup>14</sup> for  $\text{MnF}_6^{4-}$  is at least  $\pm 0.2 \cdot 10^{-4}$   $\text{cm}^{-1}$ .

Though the use of the ENDOR technique<sup>15</sup> can improve this accuracy down to  $\pm 0.01 \cdot 10^{-4}$   $\text{cm}^{-1}$ , often no ENDOR signal is detected when temperature is raised and thus this technique may not be suitable for measuring changes in  $R$  induced by thermal expansion effects.

The conclusion that  $B$  and  $C$  remain constant for  $\text{MnF}_6^{4-}$  when  $R$  varies in the range  $2.07 < R < 2.14$  Å is somewhat different to that obtained for other ions.

In this way Gardvsky *et al.*<sup>16</sup> derived for  $\text{CdTe}: \text{Co}^{2+}$  a relative decrease  $\Delta B/B \simeq 10\%$  when the applied pressure

goes from 1 atm to 2.3 GPa, which implies a change on  $R$  of 0.05 Å. A similar qualitative behavior was reported for some nickel complexes by Stephens and Drickamer.<sup>17</sup>

For both cases however the position of the three crystal-field peaks observed experimentally cannot be well fitted using an effective  $B$  parameter. Owing to this, numerical data on the variation of  $B$  with  $R$  for these systems should be regarded with caution, though it is reasonable to think that  $|\Delta B/\Delta R|$  could be higher for a more covalent system as  $\text{CdTe}: \text{Co}^{2+}$  than for  $\text{MnF}_6^{4-}$ . At variance with the later results but in accord to those for  $\text{MnF}_6^{4-}$  the theoretical calculations by Barandiaran and Pueyo<sup>18</sup> for  $\text{CrF}_6^{3-}$  predict that  $B$  is practically constant in the range  $1.73 < R < 2.11$  Å. More precisely these calculations predict that  $B$  increases only by  $\sim 1\%$  when  $R$  goes from 1.73 to 2.11 Å. The value of the exponent  $n = 4.45$  found for  $\text{MnF}_6^{4-}$  is close to the value  $n = 5$  measured by Drickamer<sup>19</sup> on NiO. In this line also, Burns and Axe,<sup>20</sup> using the semiempirical extended Hückel method, predicted values of the exponent  $n$  equal to 4.8 and 5.5 for  $\text{NiF}_6^{4-}$  and  $\text{VF}_6^{4-}$ , respectively.

As pointed out before, this proximity to the values  $n = 5$  predicted by crystal-field theory should be regarded as accidental. In fact, the difference between the energy of the one-electron levels  $e_g$  (mainly  $d_{x^2-y^2}$ ) and  $t_{2g}$  (mainly  $d_{xy}$ ) comes essentially from bonding. Owing to this, self-consistent calculations for  $\text{CrF}_6^{3-}$  and  $\text{CrF}_6^{4-}$  predict values of  $n$  equal to 1.6 and 3.2, respectively,<sup>21</sup> rather different from five. The dependence of 10 Dq upon  $R$  has been studied in the case of ionic fluoride lattices containing  $\text{Eu}^{2+}$ . Alcala *et al.*<sup>22</sup> have analyzed the experimental 10 Dq values found for  $\text{Eu}^{2+}$  in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ , and  $\text{EuF}_2$  assuming that  $R$  is always equal to the value  $R_0$  corresponding to the perfect lattice. They also find  $n \simeq 5$ . Moreover, the experimental 10 Dq values reported for  $\text{CaF}_2: \text{Eu}^{2+}$  and  $\text{BaF}_2: \text{Eu}^{2+}$  suggest that  $R$  is in fact slightly different from the corresponding  $R_0$  value. For  $\text{CaF}_2: \text{Eu}^{2+}$   $R$  should be about 0.1 Å larger than 2.36 Å while for  $\text{BaF}_2: \text{Eu}^{2+}$   $R$  is about 0.1 Å smaller than 2.69 Å. This different kind of relaxation is consistent with the ionic radii of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Eu}^{2+}$  and also with the results found for  $\text{Mn}^{2+}$  in fluoride lattices.<sup>3,23</sup>

In the later cases it has been shown<sup>3,23</sup> that if  $\text{Mn}^{2+}$  substitutes a host cation with an ionic radius higher than that of  $\text{Mn}^{2+}$  (like  $\text{Cd}^{2+}$  or  $\text{Ca}^{2+}$ ) an inward relaxation process occurs. By contrast, if the ionic radius of the host cation is smaller than 0.80 Å (as for  $\text{Zn}^{2+}$  or  $\text{Mg}^{2+}$ ) the substitution gives rise to an outward relaxation process.

Hernandez *et al.*<sup>23</sup> have also measured 10 Dq for  $\text{NaF}: \text{Eu}^{2+}$  and  $\text{KF}: \text{Eu}^{2+}$  and they derive from them a value  $n = 1.8$ , very far from the value  $n = 5$  reported by Alcala *et al.*<sup>22</sup>

To obtain  $n = 1.8$ , however, Hernandez *et al.*<sup>24</sup> assume  $R = 1.99$  Å for  $\text{NaF}: \text{Eu}^{2+}$  and  $R = 2.10$  Å for  $\text{KF}: \text{Eu}^{2+}$ . These values are difficult to accept for the following reasons:

(1) In both cases  $R$  is very far from 2.45 Å corresponding to the sum of ionic radii of  $\text{Eu}^{2+}$  and  $\text{F}^-$ . For comparison the values of  $R$  for  $\text{NaF}: \text{Mn}^{2+}$  and  $\text{KF}: \text{Mn}^{2+}$  have been derived to be  $2.15 \pm 0.02$  and  $2.17 \pm 0.02$  Å from the experimental  $A_s$  values.<sup>3</sup> Both values are in fact close to 2.13 Å despite the fact that  $R_0 = 2.67$  Å for KF and  $R_0 = 2.31$  Å for

NaF.

(2) In the case of NaF:  $\text{Eu}^{2+}$  the value  $R = 1.99 \text{ \AA}$  means an inward relaxation due to the substitution of  $\text{Na}^+$  by a cation whose ionic radius is  $0.15 \text{ \AA}$  higher. This is hard to accept, being against the behavior for  $\text{Mn}^{2+}$  in ionic fluoride lattices.<sup>3</sup>

Owing to this if we interpret the experimental values of  $10 \text{ Dq}$  for KF:  $\text{Eu}^{2+}$  and NaF:  $\text{Eu}^{2+}$  assuming an average value  $R = 2.45 \text{ \AA}$  we find that  $n$  should be higher than 2.3 provided

$$R(\text{KF: Eu}^{2+}) - R(\text{NaF: Eu}^{2+})$$

be smaller than  $0.10 \text{ \AA}$ .

In particular, if this quantity is about  $0.05 \text{ \AA}$ , the experimental  $10 \text{ Dq}$  values can also be compatible with  $n \approx 5$ .

The present results can also be of interest for understanding the small variations detected when optical spectra of  $\text{KNiF}_3$  ( $R_0 = 2.004 \text{ \AA}$ ) and  $\text{KMgF}_3$  ( $R_0 = 1.994 \text{ \AA}$ ) doped with  $\text{Ni}^{2+}$  are compared.<sup>25</sup> In this way at RT the first spin-allowed peak  ${}^3A_2 \rightarrow {}^3T_2$  appears at  $7250 \text{ cm}^{-1}$  for  $\text{KNiF}_3$  while at  $7380 \text{ cm}^{-1}$  for the latter. As this transition is identified with  $10 \text{ Dq}$ <sup>13</sup> the present shift is consistent with a slightly smaller value of  $R$  for  $\text{KMgF}_3$ :  $\text{Ni}^{2+}$  as expected. Moreover in view of the results exposed in this work one should expect that  $R(\text{KNiF}_3) - R(\text{KMgF}_3; \text{Ni}^{2+})$  is in fact less than  $10^{-2} \text{ \AA}$ . If now we interpret the shift in  $10 \text{ Dq}$  assuming Eq. (1) and taking  $n \approx 5$  then the above quantity would be equal to  $7.10^{-3} \text{ \AA}$  which is a reasonable figure.

As a final conclusion this work has pointed out the usefulness of optical measurements for deriving a reasonable value of  $R$  for metal complexes and specially for  $\text{MnF}_6^{4-}$ . This possibility is particularly attractive for the case of diluted impurities (in ionic crystals and glasses<sup>26</sup>) and also for the characterization of small precipitated phases placed inside a host lattice. In particular, evidence of the formation of such precipitated phases in  $\text{Mn}^{2+}$  doped some alkali halides have been reported.<sup>27-29</sup>

We are currently studying through the present methodology the different systems found in LiF:  $\text{Mn}^{2+}$  and NaF:  $\text{Mn}^{2+}$ .<sup>29</sup> An account of this work will be reported in the near future.

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<sup>1</sup>M. Florez, L. Seijo, and L. Pueyo, Phys. Rev. B (in press).

<sup>2</sup>A. Leblé, Thèse d'Etat, Université du Maine, 1982 and private communication.

<sup>3</sup>M. T. Barriuso and M. Moreno, Phys. Rev. B **29**, 3623 (1984).

<sup>4</sup>A. Mehra and P. Venkateswarlu, J. Chem. Phys. **47**, 2334 (1967).

<sup>5</sup>J. Ferguson, Aust. J. Chem. **21**, 307 (1968).

<sup>6</sup>J. Ferguson, H. Guggenheim, and Y. Tanabe, J. Phys. Soc. Jpn. **21**, 692 (1966).

<sup>7</sup>J. Ferguson, H. Güdel, E. Krausz, and H. Guggenheim, Mol. Phys. **28**, 893 (1974).

<sup>8</sup>D. Curie, C. Barthou, and B. Canny, J. Chem. Phys. **61**, 3048 (1974).

<sup>9</sup>Florez *et al.* (Ref. 1) point out in their work that when  $R$  increases: (a)  $B$  increases very slightly,  $(1/B)(dB/dR)$  being  $\sim 0.2 (\text{\AA})^{-1}$  for  $R = 2.12 \text{ \AA}$ . (b)  $C$  decreases very slightly  $(1/C)(dC/dR)$  being  $\sim 0.07 (\text{\AA})^{-1}$ . We have verified that this trend is true provided all the ten crystal-field states with  $S = 3/2$  be considered in the fitting but not if those arising from the  ${}^4F$  state of free  $\text{Mn}^{2+}$  are ignored. As the  ${}^4A_2(F)$ ,  ${}^4T_{12}(F)$ , and  ${}^4T_2(F)$  states of  $\text{MnF}_6^{4-}$  are very often not observed experimentally we think that it is more consistent to compare the parameters  $B$  and  $C$  derived from experimental data with those arising from a fitting to the theoretical energies of the  ${}^4T_1(G)$ ,  ${}^4T_2(G)$ ,  ${}^4A_1(G)$ ,  ${}^4E(G)$ ,  ${}^4T_2(D)$ , and  ${}^4T_1(P)$  states. Anyway, the values of  $10 \text{ Dq}$  derived in this case and given in Fig. 1 are essentially the same as those obtained by including in the fitting all the states with  $S = 3/2$ .

<sup>10</sup>H. Adachi, S. Shikawa, M. Tsukada, and S. Sugano, J. Phys. Soc. Jpn. **47**, 1528 (1979).

<sup>11</sup>S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

<sup>12</sup>S. Fraga, J. Karwowski, and K. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

<sup>13</sup>S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).

<sup>14</sup>J. J. Rousseau, A. Leblé, and J. C. Fayet, J. Phys. (Paris) **39**, 1215 (1978).

<sup>15</sup>R. K. Jeck and J. J. Krebs, Phys. Rev. B **5**, 1677 (1972).

<sup>16</sup>J. Gardavsky, A. Werner, and H. D. Hochheimer, Phys. Rev. B **24**, 4972 (1981).

<sup>17</sup>D. Stephens and H. Drickamer, J. Chem. Phys. **34**, 937 (1961).

<sup>18</sup>Z. Barandiaran and L. Pueyo, J. Chem. Phys. **80**, 1597 (1984).

<sup>19</sup>H. Drickamer, J. Chem. Phys. **47**, 1880 (1967).

<sup>20</sup>G. Burns and J. Axe, J. Chem. Phys. **45**, 4362 (1966).

<sup>21</sup>M. Bermejo and L. Pueyo, J. Chem. Phys. **78**, 854 (1983).

<sup>22</sup>R. Alcalá, D. Sardar, and W. Sibley, J. Lumin. **27**, 273 (1982).

<sup>23</sup>M. T. Barriuso and M. Moreno, Chem. Phys. Lett. **112**, 165 (1984).

<sup>24</sup>J. Hernandez, F. López, H. Murrieta, and J. Rubio, J. Phys. Soc. Jpn. **50**, 225 (1981).

<sup>25</sup>K. Knox, R. G. Shulman, and S. Sugano, Phys. Rev. **130**, 512 (1963).

<sup>26</sup>L. Feuerhelm, S. Sibley, and W. Sibley, J. Solid State Chem. **54**, 164 (1984).

<sup>27</sup>F. Rodríguez, M. Moreno, F. Jaque, and F. J. López, J. Chem. Phys. **78**, 73 (1983).

<sup>28</sup>A. de Andrés and J. M. Calleja, Solid State Commun. **48**, 949 (1983).

<sup>29</sup>M. Moreno, F. Rodríguez, J. Aramburu, F. Jaque, and F. López, Phys. Rev. B **28**, 6100 (1983).