

Zero-phonon transitions and the Stokes shift of Mn^{2+} -doped perovskites: Dependence on the metal-ligand distance

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This work reports the excitation and luminescence spectra at $T=9$ K of the Mn^{2+} -doped RbCdF_3 , RbCaF_3 , and CsCaF_3 fluoroperovskites. A Mn^{2+} concentration down to 400 ppm has been detected. The present data together with those available for $\text{KMgF}_3:\text{Mn}^{2+}$, $\text{KZnF}_3:\text{Mn}^{2+}$, KMnF_3 , and RbMnF_3 , allow us to explore the variations of the zero-phonon line (ZPL) and the Stokes shift [associated with the Mn^{2+} luminescent ${}^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ transition] along the *whole* series of cubic fluoroperovskites doped with Mn^{2+} in order to investigate their dependence with the Mn-F distance, R . The experimental variation of the ZPL energy measured in the 206–215 pm range is $E_{\text{ZPL}} = -21\,305 + 187R$ (pm). This strong dependence of ZPL upon R allows one to measure Mn-F distances along the series of fluoroperovskites with accuracies of better than 0.001 Å, thus improving by more than one order of magnitude the extended x-ray-absorption fine structure resolution. Furthermore, this sensitivity is extended down to 10^{-4} Å when we analyze the variations δR induced by pressure *in a given system*. As regards ΔE_s , the present results on Mn^{2+} -doped fluoroperovskites demonstrate an increase of the Stokes shift when R increases. This behavior is explained to be related to a Grüneisen constant $\gamma(a_{1g})$ corresponding to the symmetric mode of the complex. The value of the constant is greater than 1.9, in agreement with calculations on divalent transition-metal complexes like MnF_6^{4-} and VF_6^{4-} . The importance of the present results for the observation of luminescence through the full series of Mn^{2+} -doped fluoroperovskites is also discussed.

I. INTRODUCTION

To know the correct dependence of optical parameters upon the metal-ligand distance R is a fundamental task in the realm of transition-metal impurities in insulators. For instance, the knowledge of such a dependence enables one to detect variations δR with a resolution which can certainly be better than the best one achieved through extended x-ray-absorption fine-structure (EXAFS) experiments: ± 1 picometers (pm). Studies carried out on the absorption maxima for impurities like Mn^{2+} ,^{1–4} Cr^{3+} ,^{5–8} or Ni^{2+} (Ref. 9) in octahedral symmetry have shown that δR values of the order of 0.1 pm can be detected through the changes experienced by crystal-field transitions strongly dependent upon $10Dq$. Also, in the case of d^9 impurities with D_{4h} symmetry, changes of impurity-ligand distances around 0.1 pm can be well detected through the maxima of charge-transfer bands.^{10,11} In spite of these results little attention has been paid to the R dependence of the sharp zero-phonon lines (ZPL) which are often detected in the low-temperature emission or absorption spectra of transition-metal impurities. Preliminary results reported in Ref. 12 point out, however, that for crystal-field transitions strongly dependent upon $10Dq$, variations of the metal-ligand distance, δR , down to 0.01 pm could be detected through the corresponding changes experienced by ZPL's.

Another point related to the preceding one which also deserves investigation concerns the actual dependence upon R displayed by the Stokes shift ΔE_s . In fact, it partially determines whether luminescence will or will not be

favored by the application of external pressure.

The present work is focused on the R dependence displayed by both E_{ZPL} and ΔE_s in the octahedral MnF_6^{4-} complexes formed in fluoroperovskite lattices doped with Mn^{2+} .

The series of Mn^{2+} -doped cubic fluoroperovskites has been chosen for this work since the true Mn^{2+} -F⁻ distance was determined previously by means of three *independent* methods, and thus such systems are among the few where a proper structural characterization around the impurity has been achieved. The Mn^{2+} -F⁻ distance in that series was first established through the analysis of the experimental isotropic superhyperfine constant A_s ,¹³ and subsequently from the experimental position of the ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ band maximum.¹ In the case of RbCdF_3 and KZnF_3 , R was also measured through EXAFS.¹⁴

In this paper we report the excitation and luminescence spectra at $T=9$ K for $\text{RbCdF}_3:\text{Mn}^{2+}$, $\text{RbCaF}_3:\text{Mn}^{2+}$, and $\text{CsCaF}_3:\text{Mn}^{2+}$. Special care was paid in detecting the ZPL's due to the low Mn^{2+} concentrations of these crystals. These spectra together with those available for $\text{KMgF}_3:\text{Mn}^{2+}$, $\text{KZnF}_3:\text{Mn}^{2+}$,^{15,16} RbMnF_3 ,¹⁷ and KMnF_3 ,¹⁸ complete the whole series of fluoroperovskites and allow us to establish important correlations between the optical properties and the local structure of the MnF_6^{4-} complex.

II. EXPERIMENTAL

The single crystals of $\text{RbCdF}_3:\text{Mn}^{2+}$, $\text{CsCaF}_3:\text{Mn}^{2+}$, and $\text{RbCaF}_3:\text{Mn}^{2+}$ used in this work have already been

TABLE I. Peak energies (E_{ex} and E_{em}) and Mn-F distance (R) at $T=300$ and 9 K for the whole perovskite series. At $T=9$ K, ZPL energies for Mn^{2+} -doped perovskites and the pure exciton lines (E_1) for $RbMnF_3$ (Ref. 17) and $KMnF_3$ (Ref. 18) are also included. The values of E_{ex} and E_{em} for $RbMnF_3$ and $KMnF_3$ are taken from Ref. 47. Energies are given in cm^{-1} and distances in pm. Peak-energy errors, ΔE_{em} and ΔE_{ex} , are about ± 50 cm^{-1} , except for $KMgF_3:Mn^{2+}$ and $KZnF_3:Mn^{2+}$, where $\Delta E_{em} = \pm 100$ cm^{-1} . $\Delta E_{ZPL} = \pm 1$ cm^{-1} . For the Mn-F distance, $\Delta R = \pm 0.3$ pm in the doped perovskites.

System	$T=300$ K			$T=9$ K			
	R	E_{ex}	E_{em}	R	E_{ex}	E_{em}	E_{ZPL}
$KMgF_3:Mn^{2+}$	207.0	18 160	16 955	206.3	18 040	16 600	17 222
$KZnF_3:Mn^{2+}$	208.0	18 530	17 100	207.3	18 320	16 870	17 509
$KMnF_3$	209.5	18 900		208.7	18 800		17 883
$RbMnF_3$	212.0	19 300		211.4	19 210		18 221
$RbCdF_3:Mn^{2+}$	213.0	19 510	17 950	212.3	19 310	17 560	18 360
$RbCaF_3:Mn^{2+}$	213.2	19 560	17 920	212.5	19 290	17 610	18 428
$CsCaF_3:Mn^{2+}$	215.5	19 880	18 350	214.8	19 690	18 190	18 935

of the Mn-F distance variations measured in $RbMnF_3$ (0.6 pm),²⁰ and $KMnF_3$ (0.8 pm),²¹ as well as of the divalent cation-fluorine distance in pure crystals such as $KZnF_3$ (0.6 pm),²² $RbCdF_3$ (0.7 pm),²³ $CsCaF_3$ (0.8 pm), and $RbCaF_3$ (0.8 pm).²⁴ Although we are not able to know the precise Mn-F distance in the doped crystals,

given that the thermal expansion around the Mn^{2+} may not be necessarily that of the perfect lattice, the accuracy of these estimations is better than ± 0.3 pm, provided that the local thermal expansion of the MnF_6^{4-} complex was either twice or half the perfect lattice value.

In the observed domain of distances ($206 \leq R \leq 215$ pm), it can be noticed first that the three parameters $E_{ex}(R)$, $E_{em}(R)$, and $E_{ZPL}(R)$ increase when R increases, displaying a linear behavior (Fig. 3). The behavior of E_{ex} has been explained as follows. Within a ligand-field scheme and linear electron-phonon coupling, it can be written

$$E_{ex} = E_{ex}^0 + \hbar\omega_u \tanh(\hbar\omega_u/2k_B T). \quad (1)$$

In a first approximation $E_{ex}^0 = 6B + 5C - 10Dq$, where B , C , and $10Dq$ are the effective Racah parameters and the cubic field splitting,²⁵ respectively.

The second term of Eq. (1), which is about 10^{-2} times smaller than the first one, takes into account the phonon-assisted electric dipole character of the sideband seen in Fig. 1. We only consider one odd mode according to the analysis of $\tau(T)$ and the luminescence spectra. Theoretically,^{3,26} and experimentally,^{1,4} it has been demonstrated that B and C for MnF_6^{4-} are practically independent of R while $10Dq = KR^{-n}$. A value $n=4.7$ has been obtained experimentally² for MnF_6^{4-} .

The increase of E_{ex} on going from $KMgF_3:Mn^{2+}$ to $CsCaF_3:Mn^{2+}$ has thus to be related to the progressive decrement of $10Dq$, which in turn is induced by the host crystal involving a progressively larger lattice parameter. In fact, the room-temperature (RT) lattice parameter varies progressively from $a = 398.6$ pm for $KMgF_3$ to $a = 452.4$ pm for $CsCaF_3$.

A conspicuous feature emerging from Fig. 3 is the different slope displayed by the three experimental curves $E_{ex}(R)$, $E_{em}(R)$, and $E_{ZPL}(R)$ in the $206 < R < 215$ pm domain. More precisely, $\partial E_{ex}/\partial R = 188$ cm^{-1}/pm and $\partial E_{em}/\partial R = 172$ cm^{-1}/pm , while $\partial E_{ZPL}/\partial R = 187$ cm^{-1}/pm at $T=9$ K. A similar situation has been encountered looking at $E_{ex}(R)$ and $E_{em}(R)$ but measured at room temperature (Fig. 3).

These results have important consequences for octahe-

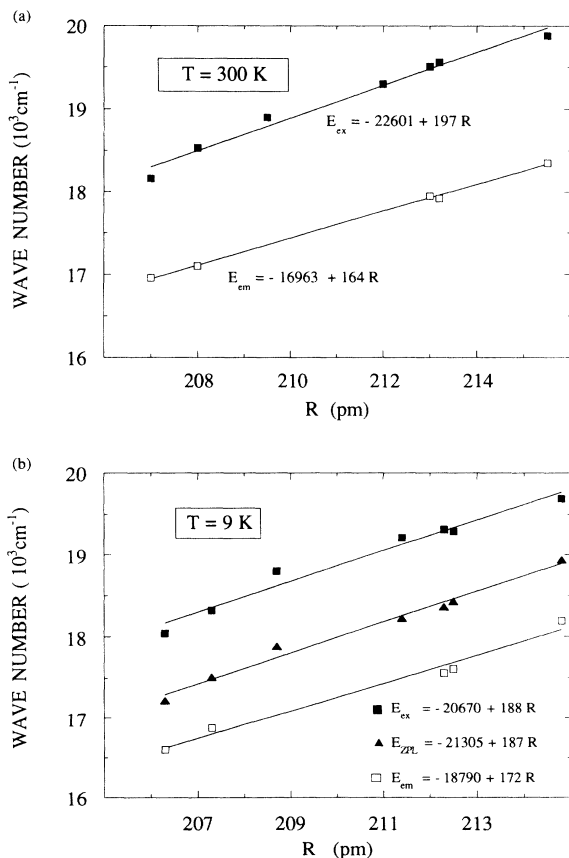


FIG. 3. Variation of the excitation and luminescence band maxima, E_{ex} and E_{em} , at $T=300$ K (a) and $T=9$ K (b) with the Mn-F distance R . The variation of the ZPL energy is given in the $T=9$ K plot. R values at 9 K correspond to the room-temperature values minus 0.7 pm (see text). Straight lines are the least-squares linear fittings. Data taken from Table I.

dral MnF_6^{4-} complexes formed in different crystals:

(1) The local Mn-F distance can be derived by measuring the excitation, the emission, or the ZPL energy. Accuracies better than 1 pm are obtained through broadbands while they are improved by one order of magnitude if the ZPL is observed (Fig. 3). This procedure is particularly important for systems where only the emission or the excitation band can be detected. This is usually found in extremely diluted systems or in concentrated materials where luminescence can be extrinsic or even absent due to the presence of excitation killers.²⁷ The R values derived for the NH_4MnF_3 perovskite at RT through the first excitation band [$E(^4T_{1g}) = 19460 \text{ cm}^{-1}$],²⁸ and for MnF_2 at 4.2 K by means of the pure exciton line ($E_1 = 18420 \text{ cm}^{-1}$),²⁹ are 212.9 and 212.3 pm, respectively. These values compare well with their respective distances, $R = 212.8$ and 212.0 pm, determined by x-ray diffraction^{28,30} and dilatometry.³¹ The latter value is just the average of 209.7 and 213.2 pm corresponding to the two short and four long Mn-F distances of the nearly MnF_6^{4-} octahedron in MnF_2 .

(2) The dependence of E_{ZPL} on R shown in Figs. 2 and 3 allows one to measure changes of the impurity-ligand distance in a given crystal down to 0.01 pm, provided that variations of the ZPL of about 10 cm^{-1} can be well detected. The sensitivity of this ZPL can be compared with that corresponding to the ruby R lines which are normally employed as probes in experiments under hydrostatic pressure.³² Using the bulk modulus $B = 700 \text{ kbar}$ for RbMnF_3 ,³³ then $\partial E_{\text{ZPL}}/\partial P = -16 \text{ cm}^{-1}/\text{kbar}$ for MnF_6^{4-} , which is 20 times higher than the variation in ruby, $\partial E_R/\partial P = -0.753 \text{ cm}^{-1}/\text{kbar}$.³⁴

(3) The plots of Fig. 3 reveal that the Stokes shift ΔE_s increases as far as R increases. Theoretically the value of this separation can be written as

$$\Delta E_s \equiv E_{\text{ex}} - E_{\text{em}} = 2\hbar\omega_u \tanh(\hbar\omega_u/2k_B T) + \Delta E_s^0, \quad (2)$$

with $\Delta E_s^0 = 2\sum_i S_i \hbar\omega_i$. Here ΔE_s^0 is the Stokes shift for an allowed transition and S_i is the Huang-Rhys factor reflecting the linear electron-phonon coupling between an electronic excited state Γ_e and a vibrational mode Γ_i whose angular frequency is just ω_i . Vibrational modes leading to nonzero values of the corresponding Huang-Rhys factor S_i follow the rule $\Gamma_e \times \Gamma_e \supset \Gamma_i$. Thus, in the case of O_h transition-metal complexes, aside from the totally symmetric a_{1g} mode, other modes of the complex can give rise to linear coupling provided the excited state is degenerate.

The first term in the right side of Eq. (2) appears in transitions whose associated sideband involves the phonon assistance by an odd mode, as happens for the ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transition of MnF_6^{4-} . Such a contribution is equal to $2\hbar\omega_u$ at low temperatures and reduces by 50% when $T \approx 300 \text{ K}$. The odd-parity phonon assistance has been shown to be the main intensity mechanism for Mn^{2+} -doped fluoroperovskites. The vibrational structure of the luminescence band together with the temperature dependence of the radiative lifetime confirm this behavior. The effective odd frequencies measured along the whole series range from $\hbar\omega_u = 220 \text{ cm}^{-1}$ for

$\text{KMgF}_3:\text{Mn}^{2+}$ (Ref. 15) to $\hbar\omega_u = 290 \text{ cm}^{-1}$ for $\text{RbCaF}_3:\text{Mn}^{2+}$.⁴ In particular, for $\text{RbCdF}_3:\text{Mn}^{2+}$, the Stokes shift measured at 9 K is equal to 1750 cm^{-1} and so $2\hbar\omega_u/\Delta E_s \approx 30\%$, taking $\hbar\omega_u = 265 \text{ cm}^{-1}$. Therefore, even at 9 K, ΔE_s is clearly dominated by ΔE_s^0 . At room temperature, ΔE_s becomes equal to 1560 cm^{-1} and thus smaller than the corresponding value measured at 9 K, in agreement with Eq. (2).

Measurements performed at RT on the pseudo-perovskite series KMgCl_3 , KCaCl_3 , RbCdCl_3 , RbCaCl_3 , CsCaCl_3 , RbSrCl_3 , and CsSrCl_3 , doped with Mn^{2+} , likely indicate that the Stokes shift ΔE_s increases with the molecular cell volume.³⁵ Although we have still not made a precise correlation between that volume and the real Mn-Cl distance of the MnCl_6^{4-} complex, the variation of $10Dq$ along this series confirms this behavior. A full analysis of both the local structure and the Stokes shift in these systems is now under way.

Having in mind the preceding analysis, the increase of ΔE_s when R increases, observed experimentally at RT and also at 9 K in fluorides, should be thus ascribed to an increase of ΔE_s^0 when R increases. An interpretation of this significant conclusion can be made through the recent microscopic analysis upon the $\Delta E_s^0(a_{1g})$ contribution to ΔE_s^0 . It has been shown²⁶ that the Huang-Rhys factor $S(a_{1g})$ associated with the symmetric a_{1g} mode increases significantly when R increases. At the same time it has been pointed out that $\Delta E_s(a_{1g})$, given by

$$\Delta E_s(a_{1g}) = 2S(a_{1g})\hbar\omega(a_{1g}), \quad (3)$$

can also increase upon increasing the metal-ligand distance R , depending on the actual value of the Grüneisen constant $\gamma(a_{1g})$, which is defined as $-3\gamma = (\partial \ln \omega / \partial \ln R)$. In fact, it has been demonstrated²⁶ that the dependence of $\Delta E_s^0(a_{1g})$ upon R , which involves the corresponding dependences displayed by both $10Dq$ and $\hbar\omega(a_{1g})$, can be written as

$$\Delta E_s^0(a_{1g}) \propto R^p, \quad \text{with } p = 6\gamma(a_{1g}) - 2(n+1). \quad (4)$$

Taking $n = 4.7$ for MnF_6^{4-} , an increase of $\Delta E_s^0(a_{1g})$ upon increasing R can be expected provided $\gamma(a_{1g}) > 1.9$. Although no experimental measurements on $\gamma(a_{1g})$ for the MnF_6^{4-} complex have been reported to our knowledge, a value $\gamma(a_{1g}) = 2.3$ is derived from the theoretical potential curve obtained by Luaña *et al.*³ for the isolated MnF_6^{4-} unit. Also, a value $\gamma(a_{1g}) = 2.9$ is obtained from the theoretical results on the VF_6^{4-} complex,³⁶ where a divalent cation is involved as well. Writing $\Delta E_s \propto R^p$, the experimental ΔE_s values measured at RT lead to $p = 5.3$. Therefore, assuming the same dependence for $\Delta E_s^0(a_{1g})$, the value $p = 5.3$ would be compatible with $\gamma(a_{1g}) = 2.8$, which is not an unreasonable figure for MnF_6^{4-} . Despite this simple picture for explaining the enhancement of the Stokes shift with R due to the a_{1g} mode, it must be stressed that the e_g mode also makes an important contribution to ΔE_s , after the results of Refs. 15 and 17.

As regards the R dependence of the latter contribution to ΔE_s [called $\Delta E_s(e_g)$], the Huang-Rhys factor $S(e_g)$

has been obtained experimentally for $\text{KMgF}_3:\text{Mn}^{2+}$, $\text{KZnF}_3:\text{Mn}^{2+}$,¹⁵ and RbMnF_3 ,¹⁷ through the reduction of the spin-orbit splitting by the Ham effect. The increase of $S(e_g)$ observed experimentally along the series $\text{KMgF}_3:\text{Mn}^{2+}$ (1.35), $\text{KZnF}_3:\text{Mn}^{2+}$ (1.5), and RbMnF_3 (1.6) justifies the increase of ΔE_s with R when coupling to the Jahn-Teller e_g mode is also considered. Recent theoretical calculations³⁷ on the Jahn-Teller coupling in the ${}^4T_{1g}(G)$ state of MnF_6^{4-} support this conclusion as they predict an R dependence of $\Delta E_s(e_g)$ very similar to that displayed by $\Delta E_s(a_{1g})$.

The R dependence of the Stokes shift ΔE_s can have a significant effect on the existence of luminescence *through the whole series* of cubic fluoroperovskites doped with Mn^{2+} . In fact, following the Dexter-Klick criterion,³⁸ the luminescence is favored by decreasing the parameter Λ_0 , defined through the equation $2\Lambda_0 = \Delta E_s^0/E_{\text{ex}}^0$. In the case of F centers in ionic solids, the luminescence is observed experimentally when $\Lambda_0 \leq 0.25$.³⁹ For the present case the increase of ΔE_s^0 upon increasing R compensates the corresponding increase of E_{ex}^0 giving rise to *near independence* of Λ from R along the whole series of fluoroperovskites. More precisely, approximating Λ_0 by Λ where $\Lambda = \Delta E_s/2E_{\text{ex}}$, measured at RT, it is found that Λ goes from 0.033 for $\text{KMgF}_3:\text{Mn}^{2+}$ (Ref. 1) to 0.038 for $\text{CsCaF}_3:\text{Mn}^{2+}$.⁴

IV. FINAL REMARKS

The present results offer a good example of the dependence of E_{ZPL} and ΔE_s upon R for a transition-metal impurity. As regards the ZPL, it has been shown that the experimental value $\partial E_{\text{ZPL}}/\partial R = +187 \text{ cm}^{-1}/\text{pm}$ found for MnF_6^{4-} opens the possibility not only for measuring metal-ligand distances but also for detecting R variations smaller than 10^{-4} \AA provided we can detect ZPL shifts of 10 cm^{-1} . The experimental value $\partial E_{\text{ZPL}}/\partial R = 187 \text{ cm}^{-1}/\text{pm}$ that in terms of pressure implies $\partial E_{\text{ZPL}}/\partial P = -16 \text{ cm}^{-1}/\text{kbar}$ is somewhat higher than the value $\partial E_{\text{ZPL}}/\partial P = -9.5 \text{ cm}^{-1}/\text{kbar}$ previously derived by Solomon and McClure from uniaxial stress ex-

periments on RbMnF_3 .¹⁷ Though no experimental data on MnF_6^{4-} in fluorides under hydrostatic pressure have been reported, measurements yield a value $\partial E_{\text{ex}}/\partial P = -26 \text{ cm}^{-1}/\text{kbar}$ for MnCl_2 , $-30 \text{ cm}^{-1}/\text{kbar}$ for MnBr_2 ,⁴⁰ and $-19.2 \text{ cm}^{-1}/\text{kbar}$ for $\text{ZnS}:\text{Mn}^{2+}$.⁴¹

The present work demonstrates experimentally that the Stokes shift associated with Mn^{2+} impurities in fluoroperovskites increases as long as R increases. This trend could, however, be different for other impurities. In fact, having in mind that the values of the exponent n for several transition-metal complexes appear to be not far from 5, a small decrement of the Grüneisen constant $\gamma(a_{1g})$, leading to $\gamma(a_{1g}) \leq 1.9$, would change the sign of this variation.

In the case of V^{2+} -doped chlorides, the analysis²⁶ of experimental results obtained by Galli, Hauser, and Güdel,⁴² indicates that p in Eq. (4) is clearly positive. This fact can be related to the value $\gamma(a_{1g}) = 2.9$ calculated by Winter and Pitzer²⁶ for VF_6^{4-} . By contrast, for CrF_6^{3-} in elpasolite lattices, the analysis carried out in Ref. 6 leads to $\gamma(a_{1g})$ values lying between 1.3 and 1.8, thus favoring a negative value for the exponent p . Recent theoretical works⁴³ also support a value of $\gamma(a_{1g}) \approx 1$. This circumstance can thus explain the slight increase undergone by the Stokes shift on passing from $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$ to $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$.⁶ In fact, as $E_{\text{ex}} = 15\,600 \text{ cm}^{-1}$ for the former system is slightly smaller than $E_{\text{ex}} = 16\,000 \text{ cm}^{-1}$ for the latter one, this would imply that R is higher for the first system given that the ${}^4A_2 \rightarrow {}^4T_2$ transition energy gives directly $10Dq$. Despite this first analysis, it is clear that more experimental data on the Stokes shift of CrF_6^{3-} in different lattices are necessary before reaching a definite conclusion on the R dependence of ΔE_s . Further work along this line is now in progress.

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