

## LETTER TO THE EDITOR

# Thermal expansion around an impurity: study of $\text{KZnF}_3:\text{Mn}^{2+}$

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**Abstract.** The thermal expansion of the  $\text{Mn}^{2+}-\text{F}^-$  bond in  $\text{KZnF}_3:\text{Mn}^{2+}$  in the 15–300 K temperature range has been studied from the variations undergone by the crystal-field spectrum. It is shown that the thermal expansion effects are clearly more significant for the  $\text{Mn}^{2+}-\text{F}^-$  distance than for the  $\text{Zn}^{2+}-\text{F}^-$  distance of the perfect lattice. In this way the linear thermal expansion coefficient  $\alpha$  for  $\text{Mn}^{2+}-\text{F}^-$  is found to be  $\alpha = (38 \pm 14)10^{-6} \text{ K}^{-1}$  at room temperature to be compared with  $\alpha = (15 \pm 0.7)10^{-6} \text{ K}^{-1}$  for the host lattice. To our knowledge this is the first time that data on thermal expansion effects around an impurity have been reported.

The properties due to a cation impurity in an ionic lattice mainly depend on the nature and number of nearest anions as well as on the true value of the impurity–ligand distance  $R$ .

However the determination of this important parameter and particularly of variations induced by temperature or pressure change is not easy.

In recent years the EXAFS technique has become a useful tool for deriving the true  $R$  distance between an ion and its nearest neighbours. Nevertheless this sophisticated technique has several inconvenient points. In particular the uncertainty involved in the obtained metal–ligand distance is usually higher than  $\pm 1 \times 10^{-2} \text{ \AA}$  which implies a lack of sensitivity for detecting variations of  $R$  induced by thermal expansion effects or applied hydrostatic pressures below about 1 GPa. On the other hand the EXAFS technique may not be useful for impurity concentrations lower than 1% [1].

Quite recently it has been stressed that good information on  $R$  can be derived from the standard optical [2] and EPR techniques [3, 4]. Though these standard tools are only useful when active impurity cations are involved it has been pointed out that  $R$  can be measured with a superior accuracy than by means of the EXAFS technique [2, 4].

In this way a recent study on the crystal field spectrum of several fluoroperovskites containing  $\text{Mn}^{2+}$  [2] has led to the conclusion that changes in  $R$  down to  $10^{-3} \text{ \AA}$  can be detected, a figure which allows us to follow the thermal expansion of the  $\text{Mn}^{2+}-\text{F}^-$  bond by looking at the variations in the optical spectrum. This Letter is devoted to a study of the thermal expansion of the  $\text{Mn}^{2+}-\text{F}^-$  bond in  $\text{KZnF}_3:\text{Mn}^{2+}$  when the temperature varies between 15 and 300 K.

To our knowledge this is the first time that data on thermal expansion effects around an impurity have been reported. The  $\text{KZnF}_3$  lattice has been chosen firstly because it

remains cubic below room temperature (RT) and secondly because of the accurate data already reported on its thermal expansion [5, 6]. The latter fact makes possible an attractive comparison between the thermal expansion undergone by the  $\text{Mn}^{2+}\text{-F}^-$  and  $\text{Zn}^{2+}\text{-F}^-$  bonds in  $\text{KZnF}_3:\text{Mn}^{2+}$ .

The basis for deriving the true  $\text{Mn}^{2+}\text{-F}^-$  distance from the crystal field spectrum is carefully discussed in [2]. Therefore we shall only present here a survey of it.

The first Hartree-Fock-Roothaan calculations carried out for the  $\text{MnF}_6^{4-}$  complex in the  $\text{RbMnF}_3$  cubic perovskite lattice for *different* values of  $R$  [7] indicate that

(i) The effect of the rest of the lattice upon the crystal-field spectrum of  $\text{MnF}_6^{4-}$  is negligible.

(ii) The theoretical electronic transitions of the  $\text{MnF}_6^{4-}$  complex involving *ten* independent Coulomb repulsion integrals can be well fitted by means of the *three usual* parameters: the effective  $B$  and  $C$  Racah parameters and the cubic field splitting  $10Dq$ .

(iii) The effective Racah parameters  $B$  and  $C$  are independent of  $R$  in a very good first approximation while  $10Dq$  depends significantly on  $R$ , being proportional to  $R^{-n}$  where  $n$  lies between 4 and 5.

The latter predictions have been confirmed by regarding the variations undergone by the optical spectrum of  $\text{MnF}_6^{4-}$  when the  $\text{Mn}^{2+}\text{-F}^-$  distance is changed [2]. This can be achieved by placing  $\text{Mn}^{2+}$  substitutionally in different cubic fluoroperovskite lattices where  $R$  is known. From this study a value of the exponent  $n = 4.5$  has been derived. Also a value  $R = 2.075 \pm 0.04 \text{ \AA}$  has been determined [2] for the  $\text{Mn}^{2+}\text{-F}^-$  bond  $\text{KZnF}_3:\text{Mn}^{2+}$  at RT in good agreement with that obtained through EXAFS [8] and EPR [4] techniques. Once  $n$  is known for  $\text{MnF}_6^{4-}$  one needs to determine experimentally the variation of  $10Dq$  with temperature for  $\text{KZnF}_3:\text{Mn}^{2+}$  in order to derive from it the corresponding variation of  $R$ .

In the excitation spectrum of cubic fluoroperovskites doped with  $\text{Mn}^{2+}$  only the first six crystal-field transitions involving excited states with  $S = \frac{3}{2}$  are detected. Among these transitions the most sensitive to  $10Dq$  is the first  ${}^6A_1 \rightarrow {}^4T_1(\text{G})$  transition. Therefore in the present work we have followed the variations undergone by the  ${}^4T_1(\text{G})$  excitation peak with temperature in order to derive from it the changes experienced in the  $\text{Mn}^{2+}\text{-F}^-$  distance.

It should be recalled here that assuming a linear electron-phonon coupling, the peak energy of a broad optical band essentially corresponds to the energy difference between the excited and ground states of the complex both calculated for the average metal-ligand distance (the so-called equilibrium distance,  $R$ , corresponding to the ground state [9, 10]). In other words, within the harmonic approximation, the first moment of the optical band is independent on the amplitude of vibrations though the second moment (the band width) is quite sensitive to it. Then changes in the first moment when temperature increases arise from anharmonicity giving rise to thermal expansion of the equilibrium distance.

The excitation and emission spectra have been recorded using a Jobin-Yvon JY 3D spectrofluorimeter improved in our laboratory. This improvement allows one to control the system and the subsequent processing of the spectra. For avoiding spurious signals in the excitation spectra suitable Oriel and Schott narrow band interference filters have been used. Temperatures down to 15 K have been achieved through a closed-cycle helium refrigerator (Air Products, Displex model CSA-202E). Good thermal contact with the sample has been ensured using a high thermal conductivity grease (Air Products Cry-Con grease).

The variation of the optical spectrum has been followed for a total of 11 different temperature values. The repeatability of measurements has been verified.

The sample used in the experiments was a KBr pellet formed with  $\text{KZnF}_3:\text{Mn}^{2+}$  powders kindly supplied by A Leblé and J J Rousseau.

In table 1 the positions of the six crystal-field excitation peaks corresponding to  $\text{KZnF}_3:\text{Mn}^{2+}$  at RT and at 15 K are reported. It can be seen that the position of the excitation peaks ( ${}^4\text{A}_1(\text{G})$ ,  ${}^4\text{E}(\text{G})$  and  ${}^4\text{E}(\text{D})$ ) which are independent of  $10\text{Dq}$  remains unchanged within our experimental accuracy. This supports that we can take the effective Racah parameters  $B$  and  $C$  as being independent of  $R$  within the domain of distances explored in our experiment.

**Table 1.** Experimental energies (in  $\text{cm}^{-1}$ ) of the emission and excitation crystal field peaks for  $\text{KZnF}_3:\text{Mn}^{2+}$  measured at room temperature and at 15 K.

	Excitation peak energy						Emission
	$6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_1(\text{G})$	${}^4\text{T}_2(\text{G})$	${}^4\text{A}_1\text{E}(\text{G})$	${}^4\text{T}_2(\text{D})$	${}^4\text{E}(\text{D})$	${}^4\text{T}_1(\text{P})$	${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$
RT	18 530	22 830	25 210	28 180	30 080	32 750	17 200
$T = 15\text{ K}$	18 350	22 590	25 210	28 220	30 080	32 830	16 670

Owing to this the changes undergone by the  ${}^4\text{T}_1(\text{G})$  or  ${}^4\text{T}_2(\text{G})$  peak energies when temperature varies between RT and 15 K should be entirely ascribed to changes in  $10\text{Dq}$ . Therefore the red shift experienced by both excitation peaks upon cooling reflects the decrease of the  $\text{Mn}^{2+}-\text{F}^-$  distance. A similar red shift is observed for the emission peak coming from the relaxed  ${}^4\text{T}_1(\text{G})$  state. In fact this peak lies at 582 nm at RT while it is found at 600 nm at 15 K. As the uncertainty in the peak position for the  ${}^4\text{T}_1(\text{G})$  excitation peak is  $\pm 0.6\text{ nm}$  it means for the present case an uncertainty for  $10\text{Dq}$  changes equal to  $\pm 20\text{ cm}^{-1}$ . From this and the dependence of  $10\text{Dq}$  on  $R^{-n}$  ( $n = 4.5$ ) we infer that the variations of  $R$  derived from the changes in the crystal field spectrum are affected by an error less than  $\pm 1 \times 10^{-3}\text{ \AA}$ .

As a guide in figure 1 the  ${}^4\text{T}_1(\text{G})$  peak energy versus temperature in the range 15–300 K is plotted. It can be seen that below  $\sim 100\text{ K}$  the energy of this peak lies always at 18 350 within experimental error while above this temperature it increases progressively.

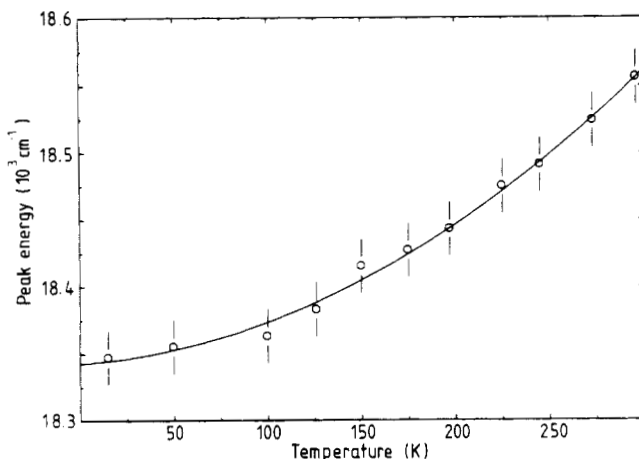
The constancy of the  ${}^4\text{T}_1(\text{G})$  peak energy below 100 K is consistent with the usual weakness of thermal expansion effects in such temperature region.

In figure 2 the value  $\Delta R(T) = R(T) - R(0)$  derived from the corresponding variations of  $10\text{Dq}$  for the  $\text{MnF}_6^{4-}$  complex in  $\text{KZnF}_3$  is reported. This curve is compared to the corresponding for the  $\text{Zn}^{2+}-\text{F}^-$  band of the perfect lattice derived from accurate x-ray diffraction measurements [5, 6].

The main conclusions contained in figure 2 are the following:

(i) The value of  $\Delta R$  (300 K) is equal to  $(12 \pm 1) \times 10^{-3}\text{ \AA}$ . This figure agrees quite well with the value  $\Delta R$  (300 K) =  $(10 \pm 3) \times 10^{-3}\text{ \AA}$  previously derived from EPR and ENDOR data for  $\text{KZnF}_3:\text{Mn}^{2+}$  and therefore it supports the present findings.

(ii) In the present case the thermal expansion of the  $\text{Mn}^{2+}-\text{F}^-$  bond is clearly different from that of the perfect lattice. In particular  $\Delta R_0$  (300 K) =  $(5.7 \pm 0.3) \times 10^{-3}\text{ \AA}$  for the  $\text{Zn}^{2+}-\text{F}^-$  bond which is nearly half the corresponding value for the  $\text{Mn}^{2+}-\text{F}^-$  bond [5, 6]. In the same vein the thermal expansion coefficient  $\alpha = (1/R)(dR/dT)$  at RT for the

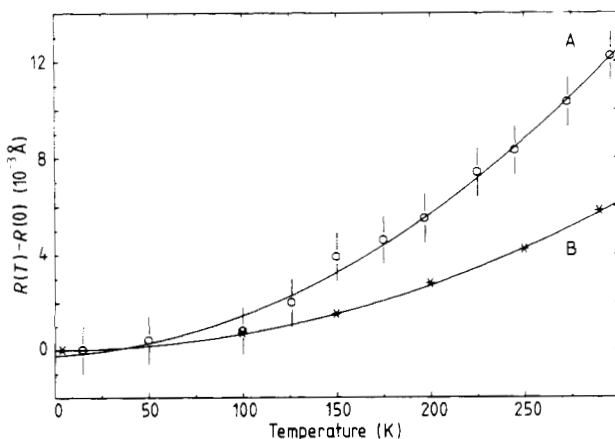


**Figure 1.** Variation of the  ${}^6A_1(S) \rightarrow {}^4T_1(G)$  peak energy for  $\text{KZnF}_3:\text{Mn}^{2+}$  with temperature in the range 15–300 K.

$\text{Mn}^{2+}-\text{F}^-$  distance is derived to be  $\alpha = (38 \pm 14) \times 10^{-6} \text{ K}^{-1}$ . This figure has to be compared with the value  $\alpha = (15 \pm 0.7) \times 10^{-6}$  reported for pure  $\text{KZnF}_3$  [5, 6].

When an impurity replaces substitutionally a host cation with smaller ionic radius it gives rise to an outward local relaxation searching an impurity–ligand distance closer to that corresponding to the ionic radii of the impurity and ligand [2, 4]. This tendency could explain why the value found for the  $\text{Mn}^{2+}-\text{F}^-$  bond in  $\text{KZnF}_3:\text{Mn}^{2+}$  is clearly higher than that of the  $\text{Zn}^{2+}-\text{F}^-$  bond if we take into account that in such a system the  $\text{Mn}^{2+}-\text{F}^-$  distance is about  $0.06 \text{ \AA}$  smaller than  $2.13 \text{ \AA}$  corresponding to the sum of ionic radii of  $\text{Mn}^{2+}$  and  $\text{F}^-$ .

In conclusion this work has stressed the usefulness of optical measurements for deriving from them the impurity–ligand distance changes induced by thermal expansion



**Figure 2.** Changes of  $\Delta R = R(T) - R(0)$  for  $\text{Mn}^{2+}-\text{F}^-$  (A) and  $\text{Zn}^{2+}-\text{F}^-$  (B) bond distances in  $\text{KZnF}_3$  doped  $\text{Mn}^{2+}$  as a function of temperature. (A)  $R(0) = 2.064 \pm 0.004 \text{ \AA}$  (derived from the excitation spectrum at 15 K.) (B)  $R(0) = 2.0207 \text{ \AA}$  (taken from [5]).

effects or applied hydrostatic pressures. Also it offers good evidence that the thermal expansion around an impurity can be quite different from that of the perfect lattice.

Further work along these lines is now in progress.

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