An insight into the local $O_h \rightarrow T_d$ instability in BaF$_2$:Mn$^{2+}$

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Abstract. While most complexes in fluorite-type lattices (CaF$_2$, SrF$_2$, CdF$_2$) containing Mn$^{2+}$ impurities remain cubic at all temperatures, electron paramagnetic resonance (EPR) measurements have shown that the one in BaF$_2$ is tetrahedral below 50K. This surprising behaviour is intrinsic to the centre and not associated to any close defect or pure lattice phase-transition. Through the use of density functional (DFT) calculations we show that the distortion is linked to the unexpected low force constant along the tetrahedral distortion mode with $a_{2u}$ symmetry in these complexes and the large metal-ligand distance existing in BaF$_2$:Mn$^{2+}$. Ultimately, these facts reflect that, for substitutional impurities in fluorite-type crystals, the ligand-ligand interaction is dominant over the metal-ligand one.

1. Introduction
Magnetic resonance data [1,2] on BaF$_2$:Mn$^{2+}$ reveal the existence of a surprising phenomenon not observed either in MF$_2$:Mn$^{2+}$ (M: Ca, Sr, Cd) or in Mn$^{2+}$ doped cubic fluoroperovskites. Indeed electron paramagnetic resonance (EPR) spectra of BaF$_2$:Mn$^{2+}$ detected at temperatures $T>50$ K are consistent with a cubic local symmetry around an isolated Mn$^{2+}$ impurity as the one found in MF$_2$:Mn$^{2+}$ (M: Ca, Sr, Cd) at and below room temperature [3]. However this situation is not longer true for BaF$_2$:Mn$^{2+}$ because below 50 K the superhyperfine (shf) interaction shows the existence of a local tetrahedral symmetry involving two different Mn$^{2+}$-F bonds [1,2]. This fact just means that at $T=0$K the cube involving eight F ions in the corners is distorted giving rise to four short Mn$^{2+}$-F bonds with a length equal to $R_s$ and four long bonds with a length equal to $R_l$ (figure 1). The isotropic superhyperfine constants, $A_s$(s) and $A_s$(l) associated with short and long bonds respectively have been measured to be equal to $A_s$(s)=29.1 MHz and $A_s$(l)=10.5 MHz [1,2]. From these values it has been estimated $R_s=0.25$ Å [4]. All these conclusions were supported by subsequent electron nuclear double resonance (ENDOR) spectra obtained on BaF$_2$:Mn$^{2+}$ from which no evidence of any nearby defect to an isolated Mn$^{2+}$ impurity was encountered [2].

The $O_h \rightarrow T_d$ instability is puzzling first because there is not any structural phase transition in the host lattice below 1200 K at zero pressure to which the phenomenon could be attributed [5]. On the other hand such instability involves the softening of a local $a_{2u}$ mode (figure 1) which has a stretching character.
The present work is aimed at clearing out the origin of the $O_h \rightarrow T_d$ instability observed in BaF$_2$:Mn$^{2+}$ by means of density functional theory (DFT) calculations carried out on this system as well as on CaF$_2$:Mn$^{2+}$ and SrF$_2$:Mn$^{2+}$. In Section 2 a short outline of the methods of calculation employed in this work is provided while the main results are shown in section 3. A short account of the main conclusions and some final remarks are given in the last section.

2. Computational details
Due to the strong localization of the active electrons in the MnF$_8^6$ complex we have been able to simulate the system using the cluster approximation. The main results have been obtained employing a 21-ion cluster (MnF$_8$Ba$_{12}$). Further calculations have been carried out in a 57-ion cluster (MnF$_8$Ba$_{12}$F$_{24}$Ba$_6$). The validity of both clusters to study impurities in fluorite-type crystals has been already checked in previous works [6, 7]. The effect of the long-range potential due to the rest of the lattice over the clusters has been introduced by including a large number of point charges at the ions' positions. Finally, and due to the presence of heavy atoms like barium and transition metals like manganese in the clusters, we checked the effect of scalar relativistic corrections in our calculations which were negligible.

3. Results and Discussion
In a first step the value of the equilibrium Mn$^{2+}$-F distance, $R$, for CaF$_2$:Mn$^{2+}$ and SrF$_2$:Mn$^{2+}$ has been calculated. These values are reported in Table 1 and compared to the M$^{2+}$-F distance (M:Ca,Sr) of the host lattice designated by $R_0$. It is worthwhile to remark that the value $R = 2.29$ Å derived for CaF$_2$:Mn$^{2+}$ essentially matches the figure $R = 2.28 \pm 0.01$ Å measured by extended x-ray absorption fine structure (EXAFS) technique [14] and previous calculations by Pascual et al. [15]. Along this line the $R$ values collected in Table 1 are not far from $R = 2.27$ Å and $R = 2.31$ Å estimated from the analysis of the experimental isotropic superhyperfine (shf) constant, $A$, for CaF$_2$:Mn$^{2+}$ and SrF$_2$:Mn$^{2+}$ respectively [16]. Comparing the $R_0$ (the cation-anion distance in the pure lattice) and $R$ values
gained in Table 1 in MF$_2$:Mn$^{2+}$ (M = Ca, Sr) it can be noted that the M$^{2+}$ → Mn$^{2+}$ substitution gives rise to an inwards relaxation. Bearing in mind the ionic radii of Mn$^{2+}$ and F$^-$ as well as Pauling's rules that take into account the influence of the coordination number upon the equilibrium distance this fact is quite reasonable. Accordingly, when a Mn$^{2+}$ ion is surrounded by eight F$^-$ ions one would expect an equilibrium distance, R$_e$, close to 2.22 Å. The calculated R values for MF$_2$:Mn$^{2+}$ (M = Ca, Sr) in Table 1 thus imply a deviation of less than 5.5% with respect to R$_e = 2.22$ Å.

For the sake of clarity the R value calculated for BaF$_2$:Mn$^{2+}$ imposing a hexahedral symmetry is also reported in Table 1. The obtained value R = 2.47 Å thus implies a huge deviation (12%) with respect to R$_e = 2.22$ Å. It is worth noting that this shift is certainly bigger than that found in the case of Mn$^{2+}$ doped cubic fluoroperovskites entering an octahedral position where the difference between the obtained R values and R$_e = 2.13$ Å never exceeds 4% [17].

In a second step, the frequencies $\nu$(a$_{1g}$) and $\nu$(a$_{2u}$), corresponding, respectively, to the symmetric a$_{1g}$ local mode and to the a$_{2u}$ mode (depicted in figure 1), have been derived. In the case of the BaF$_2$:Mn$^{2+}$ the $\nu$(a$_{1g}$) and $\nu$(a$_{2u}$) values reflect distortions around a forced hexahedral symmetry. From the results gathered in Table 1 and figure 2 it can be noticed that:

i) The calculated $\nu$(a$_{1g}$) values are always found to be well above zero.

ii) Despite the a$_{2u}$ mode has also a stretching character the calculated $\nu$(a$_{2u}$) value for MF$_2$:Mn$^{2+}$ (M = Ca, Sr) is found to be substantially smaller than the figure corresponding to $\nu$(a$_{1g}$).

iii) Similarly to what is observed for stretching local modes [18,19] under hydrostatic pressure a reduction on R favours an increase of both $\nu$(a$_{1g}$) and $\nu$(a$_{2u}$).

iv) In the case of BaF$_2$:Mn$^{2+}$, $\nu$(a$_{2u}$) is found to be imaginary, implying that the equilibrium geometry is not cubic but tetrahedral in agreement with experimental EPR and ENDOR data [1,2].

| Table 1. Metal-ligand distance (R) and stretching frequencies, $\nu$(a$_{1g}$) and $\nu$(a$_{2u}$), of the MnF$_8$ complex as calculated using DFT in different lattices. The cation-anion distance in the pure lattice (R$_0$) is also shown for comparison. |
|-----------------|-----------------|-----------------|
|                 | CaF$_2$         | SrF$_2$         | BaF$_2$         |
| R$_0$ (Å)       | 2.37            | 2.51            | 2.69            |
| R (Å)           | 2.29            | 2.34            | 2.47            |
| $\nu$(a$_{1g}$) (cm$^{-1}$) | 357             | 326             | 267             |
| $\nu$(a$_{2u}$) (cm$^{-1}$) | 168             | 132             | 59              |

Figure 2. Variation of K(a$_{2u}$) with the metal-ligand distance.
Looking at table 1 it appears that the $a_{2u}$ instability in BaF$_2$:Mn$^{2+}$ is somewhat related to the high $R$ value embodied in table 1. Let us write the two $\nu(j)$ frequencies ($j$: $a_{1g}$, $a_{2u}$) as

$$\nu(j) = \frac{1}{2\pi} \sqrt{\frac{K(j)}{M_L}}$$

where $M_L$ denotes the ligand mass. The value of the calculated $K(a_{2u})$ force constant for MF$_2$:Mn$^{2+}$ ($M$ = Ca, Sr) is portrayed in figure 2. It can be noticed that a simple linear interpolation of such values leads to a small but negative $K(a_{2u})$ value when $R = 2.47$ Å.

A central matter in the present analysis is thus to understand why $\nu(a_{2u})$ is significantly smaller than $\nu(a_{1g})$ for a given system despite both modes have a stretching character. Some insight on this key issue is gained writing both $K(a_{2u})$ and $K(a_{1g})$ approximately in terms of the two-body metal-ligand, $K_{ML}$, and ligand-ligand, $K_{LL}$, force constants which appear in a phenomenological description of vibrations considering only central forces[20]. The relation between $K(a_{2u})$ and $K(a_{1g})$ and $K_{ML}$ and $K_{LL}$ can easily be derived to be

$$K(a_{1g}) = K_{ML} + 2K_{LL}$$

$$K(a_{2u}) = K_{ML}$$

(2)

It is worth noting that $K(a_{2u})$ does not depend on $K_{LL}$. This fact merely reflects that the distance between two closest ligands is unmodified through a small $a_{2u}$ distortion. Consider for instance the ligands placed initially at $(r,r,r)$ and $(-r,r,r)$ which under the $a_{2u}$ distortion their coordinates become equal to $(r+\varepsilon,r+\varepsilon,r+\varepsilon)$ and $(-r+\varepsilon,r-\varepsilon,r-\varepsilon)$ where $\varepsilon \ll r$. The change of distance between the two ligands thus remains unchanged to first order of $\varepsilon$. Moreover if the $\nu(a_{1g})$ and $\nu(a_{2u})$ values obtained for MF$_2$:Mn$^{2+}$ ($M$ = Ca, Sr) in table 1 are analysed by means of Eqs (1) and (2) it turns out that $K(a_{1g})$ is dominated by the ligand-ligand contribution, $K_{LL}$, which does not play any role in the $a_{2u}$ mode. For instance for SrF$_2$:Mn$^{2+}$ the analysis of $\nu(a_{1g})$ and $\nu(a_{2u})$ values collected in table 1 lead to a ratio $K_{LL}/K_{ML} = 2.6$. Therefore in fluorite-type lattices the dominant contribution to the frequency of stretching modes is not $K_{ML}$ but $K_{LL}$, a fact which is thus contrary to what happens in cubic lattices with octahedral coordination[21].

A better insight on the instability in BaF$_2$:Mn$^{2+}$ can be gained plotting the ground state energy, $E$, as a function of the distortion coordinate $Q(a_{2u})$, whose absolute value is given by $\sqrt{2}(R_L - R_S)$. The result, displayed in figure 3, reveals the existence of a shallow double well with minima located at $Q(a_{2u}) \approx \pm 0.41$ Å. This value implies a figure $R_L - R_S = 0.29$ Å which is not far from the previous estimations derived from the experimental isotropic shf constant. As expected form the results displayed in figure 2 we have verified that the tiny barrier (of about 50 cm$^{-1}$) shown in figure 2 disappears if a small pressure that reduces the lattice parameter of BaF$_2$ by only 1.5% is applied.

**Figure 3.** Cross section of the adiabatic energy surface along the $a_{2u}$ distortion and the vibrational levels associated to it.
Despite the energy barrier obtained at zero pressure is only $\sim 50 \text{ cm}^{-1}$ it should be pointed out that the lowest vibrational state is found to be essentially localized in a given well. By contrast in all excited states the calculated wavefunction is delocalized. The relevance of this fact in connection with the $T_d \rightarrow O_h$ transition observed upon rising the temperature has recently been discussed [22].

4. Conclusions and Final Remarks

The present study has shown that the $a_{2u}$ instability observed in BaF$_2$:Mn$^{2+}$ is favoured by two factors. On one hand the Mn$^{2+}$-$F^-$ distance for a MnF$_8^{6-}$ complex in BaF$_2$ keeping the $O_h$ symmetry is calculated to be unusually high. On the other hand $\nu(a_{2u})$ is not dependent on the ligand-ligand force constant, $K_{LL}$, which is clearly the dominant one for host lattices with fluorite structure.

It should be emphasized that the $a_{2u}$ instability cannot properly be understood considering Mn$^{2+}$ and F$^-$ as rigid ions. In fact, for this kind of phenomena arising from the so called pseudo Jahn-Teller effect it is crucial to take into account the changes in electronic density which take place from $Q(a_{2u}) = 0$ to a distorted geometry involving $Q(a_{2u}) \neq 0$ [23, 6, 22].

The present results can also be of interest in the realm of structural phase transitions in pure insulating materials. Indeed it has been pointed out [24] that the occurrence of an on site instability favours the existence of a structural phase transition.

According to the results displayed in figure 3 the $a_{2u}$ instability can also have an important influence for understanding the isotropic superhyperfine constant on the cubic phase. Indeed the distance between a given F$^-$ ligand ion and the Mn$^{2+}$ impurity would experience a fluctuation of at least $\pm 0.15 \text{ Å}$ with respect to its average value. This relevant fact could explain why $A_{c} = 21.2 \pm 1.5$ MHz measured for BaF$_2$:Mn$^{2+}$ at room temperature is identical to $A_{c} = 22.2 \pm 0.3$ MHz for SrF$_2$:Mn$^{2+}$ within experimental uncertainties [3]. Work on this relevant issue and on the influence of the vibronic admixture with excited states on the value of $\nu(a_{2u})$ for BaF$_2$:Mn$^{2+}$, CaF$_2$:Mn$^{2+}$ and SrF$_2$:Mn$^{2+}$ is currently under way.

Acknowledgements

The support by the Spanish Ministerio de Ciencia y Tecnología under project FIS2006-02261 is acknowledged.

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