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Proceedings of the International School and Conference on Optics and  
Optical Materials, ISCOM07, Belgrade, Serbia, September 3–7, 2007

## Geometry of the ${}^4T_{2g}$ Excited State in $\text{Cs}_2\text{SiF}_6:\text{Mn}^{4+}$

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The aim of this paper is to calculate the equilibrium displacements of the  ${}^4T_{2g}$  potential surface minimum from the ground state along the  $a_{1g}$  and  $e_g$  Jahn–Teller active modes for the octahedral  $[\text{MnF}_6]^{2-}$  cluster obtained by doping  $\text{Mn}^{4+}$  ions in  $\text{Cs}_2\text{SiF}_6$  host crystal. The equilibrium displacements in normal and Cartesian coordinates were estimated from force constants of  $[\text{MnF}_6]^{2-}$  cluster and Huang–Rhys factors associated with the Jahn–Teller stabilization energy. A net equatorial expansion and an axial stretching of the geometry of the  $[\text{MnF}_6]^{2-}$  cluster in first  ${}^4T_{2g}$  excited state, as combined effect of the  $a_{1g}$  and  $e_g$  displacements, were demonstrated.

PACS numbers: 71.70.Ej, 63.20.Kr, 63.70.+h

### 1. Introduction

$\text{Cs}_2\text{SiF}_6 : \text{Mn}^{4+}$  belongs to a larger category of crystals,  $A_2M^{IV}F_6 : \text{MnF}_6^{2-}$  compounds ( $A^I = \text{Cs}$ ,  $M^{IV} = \text{Si}$ ,  $\text{Ge}$ ), which have been investigated from both experimental and theoretical point of view [1–3].  $\text{Mn}^{4+}$  has  $3d^3$  electron configuration, like  $\text{V}^{2+}$  or  $\text{Cr}^{3+}$ , that is why it has a special combination of spin-doublet and spin-quartet states in the octahedral crystal field, which allows to get either sharp luminescence lines (in the case of a strong crystal field, when the first excited state is the  ${}^2E_g$  doublet) or broadband luminescence (in the case of a weak crystal field with the  ${}^4T_{2g}$  quartet being the first excited state).

In  $\text{Cs}_2\text{SiF}_6 : \text{Mn}^{4+}$  crystal, the cluster  $[\text{MnF}_6]^{2-}$  is weakly coupled to the lattice with quite sharp spectral features [1] because the cluster octahedron does not share faces, edges, or corners with neighboring octahedral.

The spectra of  $\text{Mn}^{4+}$  ions in various crystals are strongly influenced by the coupling between the phonons of the host matrix and the electronic state of the impurity ions. The adiabatic potentials corresponding to the ground and excited states of  $\text{Mn}^{4+}$  ions in the  $[\text{MnF}_6]^{2-}$  cluster have different geometries. This leads

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to a relative displacement of their potential energy surface along the  $a_{1g}$  and  $e_g$  normal vibration modes of the cluster.

In Ref. [4] we have studied the influence of the Jahn–Teller effect on the first excited state of  $Mn^{4+}$  doped in  $Cs_2SiF_6$  crystal and calculated the Jahn–Teller stabilization energy. The next step is to find out the equilibrium displacements of the  ${}^4T_{2g}$  potential surface minimum from the ground state along the  $a_{1g}$  and  $e_g$  Jahn–Teller active modes.

The aim of this paper is a theoretical analysis of the geometry of the  ${}^4T_{2g}$  excited state in  $Cs_2SiF_6:Mn^{4+}$  crystal, which is influenced by its coupling with the total symmetric  $a_{1g}$  and double degenerated  $e_g$  normal vibrations of the  $[MnF_6]^{2-}$  cluster due to the dynamic Jahn–Teller effect.

## 2. Experimental support

This paper has as started point the optical spectra of the  $Cs_2SiF_6$  crystal, which was obtained by Seijo et al. [5] and our earlier theoretical analysis regarding the Jahn–Teller effect on the  ${}^4T_{2g}$  energy level of  $Mn^{4+}$  doped in  $Cs_2SiF_6$  [4].

The space group to which  $Cs_2SiF_6$  crystal belongs is  $Fm\bar{3}m - O_h^5$  (antifluorite), each silicon ion occupies a position with  $O_h$  site symmetry. The distance between the silicon ion and each of the six fluorides is 1.695 Å [5]. Doping the crystal with  $Mn^{4+}$  ions, these will substitute the silicon ions and the distances  $Mn^{4+}-F^-$  will be 1.74 Å [5]. Between the  $[MnF_6]^{2-}$  cluster and the rest of the lattice it is a very weak connection, this being justified by the following features: the sharpness of the vibrational lines, the near absence of lines due to  $[SiF_6]^{2-}$  octahedral, the weakness of acoustic phonon bands and the host independence of the spectra [5].

The  $Mn^{4+}$  ion has three  $3d$  electrons and all its visible and near ultraviolet spectra are due to the  $d-d$  transitions.

Seijo et al. [5] have established that the  ${}^4T_{2g}$  state undergoes spin–orbit splitting into  $\Gamma_7$ ,  $\Gamma_8^b$ ,  $\Gamma_6$ , and  $\Gamma_8^a$  components. These have relative energies: 0, 12, 68, 64. Using the crystal field theory, previously [4] we calculated the theoretical values for these four components of the  ${}^4T_{2g}$  state. The obtained relative energies are: 67.5, 273.7, and 269.6, respectively. We can notice differences between the theoretical and experimental data. These differences were explained [4] by taking into account the dynamical Jahn–Teller effect.

The theoretical and experimental data fit for a Ham reduction factor of  $\gamma = 0.28$  gave a Jahn–Teller stabilization energy of  $E_{JT} = 422 \text{ cm}^{-1}$  [4].

## 3. Electron–phonon coupling in the ${}^4T_{2g}$ excited state

The  $[MnF_6]^{2-}$  octahedron cluster has the  $a_{1g}$ ,  $e_g$ , and  $t_{2g}$  Jahn–Teller active normal vibration modes.

Using the dynamical ligand field model [6, 7] we evaluated, in the linear approximation of this model, the vibration coupling constants between these normal

modes and the  ${}^4T_{2g}$  electronic state. These constants have the following explicit expressions [7]:

$$\left\langle {}^4T_{2g} \left\| \frac{\partial V}{\partial Q_{a_{1g}}} \right\| {}^4T_{2g} \right\rangle = -\frac{50Dq}{\sqrt{6}R_0}, \quad (1)$$

$$\left\langle {}^4T_{2g} \left\| \frac{\partial V}{\partial Q_{e_g}} \right\| {}^4T_{2g} \right\rangle = -\frac{25Dq}{\sqrt{3}R_0}, \quad (2)$$

$$\left\langle {}^4T_{2g} \left\| \frac{\partial V}{\partial Q_{t_{2g}}} \right\| {}^4T_{2g} \right\rangle = \frac{4\sqrt{3}Dq}{7R_0} \left( \frac{5}{3} - \frac{3}{\eta} \right), \quad (3)$$

where  $Q_{a_{1g}}$ ,  $Q_{e_g}$ ,  $Q_{t_{2g}}$  are the normal coordinates for the  $a_{1g}$ ,  $e_g$  and respectively  $t_{2g}$  active modes,  $Dq$  is the crystal field strength and  $R_0$  is the equilibrium distance between the central ion and ligand. The parameter  $\eta$  is related to the angular overlap model (AOM) parameters  $e_\sigma$  and  $e_\pi$  [8] ( $e_\delta = 0$ ):

$$\eta = \frac{3}{5} \frac{3 - 4e_\pi/e_\sigma}{1 + e_\pi/e_\sigma}. \quad (4)$$

From a two-dimensional spectrochemical series [9] the ratio of the AOM parameters  $e_\sigma$  and  $e_\pi$  for  $[MnF_6]^{2-}$  is obtained:  $e_\sigma/e_\pi \approx 0.31$ . Using this value in (4) it results that  $\eta \approx 0.8$ . Introducing the values of  $Dq = 2162.6 \text{ cm}^{-1}$  [5],  $R_0 = 1.695 \text{ \AA}$  [5] and  $\eta \approx 0.8$  in (1), (2) and (3) we obtain the following values for the vibration coupling constants:

$$\left\langle {}^4T_{2g} \left\| \frac{\partial V}{\partial Q_{a_{1g}}} \right\| {}^4T_{2g} \right\rangle = -0.5178 \times 10^{-8} \text{ N}, \quad (5)$$

$$\left\langle {}^4T_{2g} \left\| \frac{\partial V}{\partial Q_{e_g}} \right\| {}^4T_{2g} \right\rangle = -0.366 \times 10^{-8} \text{ N}, \quad (6)$$

$$\left\langle {}^4T_{2g} \left\| \frac{\partial V}{\partial Q_{t_{2g}}} \right\| {}^4T_{2g} \right\rangle = -0.5231 \times 10^{-9} \text{ N}. \quad (7)$$

As can be seen, the coupling of  ${}^4T_{2g}$  electronic state to the  $t_{2g}$  mode is ten times weaker than that to the  $a_{1g}$  and  $e_g$  modes. That is why we take into account just the first two vibration modes.

Using  $E_{JT} = 422 \text{ cm}^{-1}$  [4] obtained previously we estimate the Huang–Rhys parameters  $S$  using [10]:

$$S = \frac{E_{JT}}{\hbar\omega_{eg}}. \quad (8)$$

For  $\hbar\omega_{eg} = 510 \text{ cm}^{-1}$  we obtained  $S_{e_g} = 0.83$ . The value of the Huang–Rhys parameter  $S_{a_{1g}} = 2.75$  is taken from [5].

#### 4. Geometry of the ${}^4T_{2g}$ excited state in $Cs_2SiF_6:Mn^{4+}$

Next we will calculate the equilibrium displacements of  ${}^4T_{2g}$  from the ground state along the  $a_{1g}$  and  $e_g$  active modes of the cluster  $[MnF_6]^{2-}$  using the following equation [11]:

$$|\Delta Q_i|_{eg} = \sqrt{\frac{2S_i h \nu_i}{f_i}}. \quad (9)$$

Here  $Q_i$  denotes the  $i$ -th normal mode,  $f_i$  — the force constants of the harmonic vibrations and  $S_i$  the Huang–Rhys factors.

We determined the  $f_i$  constants using the force constants and kinetic energy (FG) matrix method for the octahedral  $[\text{MnF}_6]^{2-}$  cluster [12]. Taking  $h\nu_{a_{1g}} = 595 \text{ cm}^{-1}$  and  $h\nu_{e_g} = 510 \text{ cm}^{-1}$  [13] we obtained  $f_{a_{1g}} = 294.45 \text{ N/m}$  and  $f_{e_g} = 216.33 \text{ N/m}$ . Using the above Huang–Rhys factors, the force constants and Eq. (9) we obtained  $|\Delta Q_{a_{1g}}| = 0.1486 \text{ \AA}$  and  $|\Delta Q_{e_g}| = 0.08816 \text{ \AA}$ . The connection between the  $Q$  displacements in normal coordinates and the Cartesian coordinates [14] is

$$\begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \sqrt{\frac{2}{3}} - \sqrt{\frac{1}{3}} - 1 \\ \sqrt{\frac{2}{3}} - \sqrt{\frac{1}{3}} + 1 \\ \sqrt{\frac{2}{3}} - \sqrt{\frac{4}{3}} + 0 \end{pmatrix} \begin{pmatrix} \Delta Q_{a_{1g}} \\ \Delta Q_{e_{g\theta}} \\ \Delta Q_{e_{g\epsilon}} \end{pmatrix}. \quad (10)$$

From this equation  $x = y = 0.086 \text{ \AA}$  and  $z = 0.112 \text{ \AA}$ .

## 5. Conclusions

Our geometry study of the excited state  ${}^4T_{2g}$  of  $\text{Cs}_2\text{SiF}_6:\text{Mn}^{4+}$  begun with the calculation of the coupling between the  $a_{1g}$  and  $e_g$  vibration modes and the  ${}^4T_{2g}$  electronic state of  $\text{Mn}^{4+}$  ions.

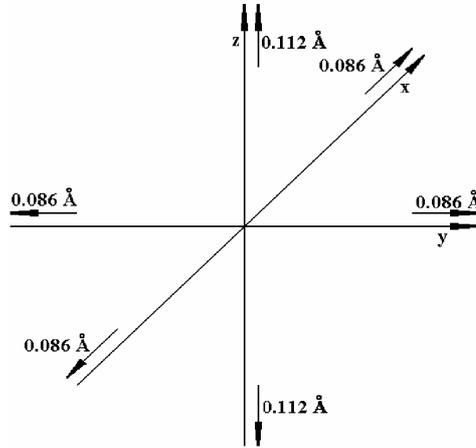


Fig. 1. Distortion of the  $[\text{MnF}_6]^{2-}$  cluster in the  ${}^4T_{2g}$  excited state with respect to the ground state.

Using the value of the Jahn–Teller stabilization energy  $E_{JT}$ , the Huang–Rhys parameters  $S_{e_g}$  and  $S_{a_{1g}}$ , the frequency for the two vibration modes  $h\nu_{a_{1g}}$  and  $h\nu_{e_g}$ , we calculated, using the FG matrix method, the force constants  $f_{a_{1g}}$  and  $f_{e_g}$ .

Finally we determined the equilibrium displacements of the  ${}^4T_{2g}$  state from the ground state both in normal and Cartesian coordinates. The obtained values are:  $|\Delta Q_{a_{1g}}| = 0.1486 \text{ \AA}$  and  $|\Delta Q_{e_g}| = 0.08816 \text{ \AA}$ , respectively  $x = y = 0.086 \text{ \AA}$  and  $z = 0.112 \text{ \AA}$ .

The combined effect of the  $a_{1g}$  and  $e_g$  displacements is equatorial expansion and axial stretching (Fig. 1).

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