Electron-phonon Coupling in the $^4T_{2g}$ Excited Electron State of Cs$_2$GeF$_6$:Mn$^{4+}$

N. M. Avram and M. G. Brik

Department of Physics, West University of Timisoara, Bd. V. Parvan 4, Timisoara 300223, Romania

$^a$ Fukui Institute for Fundamental Chemistry, Kyoto University, 34–4, Takano Nishihiraki-cho, Sakyo-ku, Kyoto 606–8103, Japan

Reprint requests to Dr. M. G. B., e-mail brik@fukui.kyoto-u.ac.jp

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In the present paper we report on an analysis of the fine structure of the first excited quartet $^4T_{2g}$ of Mn$^{4+}$ ions which occupy the octahedral site in the Cs$_2$GeF$_6$ host crystal. The dynamic $^4T_{2g} \otimes (e_g + t_{2g})$ Jahn–Teller effect is considered in details, including the Ham effect of the reduction of the spin-orbit splitting and displacements of the ligands due to the combined effect of the $a_{1g}$ and $e_g$ normal modes of the [MnF$_6$]$^{2-}$ octahedral complex. The electron-phonon coupling constants are evaluated using the experimental spectroscopic data. The value of the Jahn–Teller stabilization energy $E_{JT} = 438$ cm$^{-1}$ for the considered complex is estimated from both the Ham effect and the potential energy surface of the $^4T_{2g}$ excited state.

Key words: Laser Crystals; Electron-phonon Coupling; Jahn–Teller Effect.

1. Introduction

Transition metal ions as optical active centers in various crystals have been the subject of a great number of experimental and theoretical studies (e. g. [1, 2] and references therein). Electronic transitions between the energy levels of their external unfilled 3d shell give rise to intense and broad (or sharp) luminescence bands depending on the spin and symmetry of the states involved in the transitions and the dynamics of the environment surrounding the active ions in the crystal.

The host materials doped with transitional metal ions with 3d$^3$ electron configuration (V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$) have received considerable attention, both experimental and theoretical, during the development of the crystal and ligand field theories [3 – 6]. The reason is that the 3d$^3$ electron shell has a very attractive combination of spin-doublet and spin-quartet states in the octahedral crystal field, which allows for getting 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). Among different possible hosts for these ions, chloride and fluoride crystals are especially interesting from the spectroscopic point of view, since the phonon cut-off energy is rather low, causing the emission life-time of the excited state to be greater than, for example, for oxides crystals.

V$^{2+}$ ions typically show a high quantum efficiency of fluorescence in different host crystals. Their spectroscopic and lasing properties in doped halide crystals have been studied in [7 – 9]. Cr$^{3+}$ ions as active centers in tunable laser materials and sensitizers in rare-earth co-doped host materials have been described in [10 – 12].

The vibronic spectra and lattice dynamics of A$^2_1$M$^{IV}$/F$_6$:MnF$_6^{2-}$ compounds (A$^1_1 = K$, Rb, M$^{IV}$ = Si; A$^1_1 = Cs$, M$^{IV}$ = Si, Ge) have been investigated from both experimental and theoretical points of view [13 – 16]. All spectra of the V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$ ions in various crystals are strongly influenced by a coupling between the phonons of the host matrix and the electronic state of the impurity ion.

The vibronic interaction as dynamical Jahn–Teller effect in the $^4T_{2g}$ excited state has been investigated for different combinations of impurity ions and host crystals: by Sturge [17] for KMgF$_3$:V$^{2+}$, Bevilacqua et al. [18] for ZnS:V$^{2+}$ and ZnSe:V$^{2+}$, Avram and Brik [19] for CsCaF$_3$:V$^{2+}$, Güdel and Snellgrove [20] for Cs$_2$NaInCl$_6$:Cr$^{3+}$, Pillai et al. [21] for KZnF$_3$:Cr$^{3+}$, Knochenmuss et al. [22] for CsNaYCl$_6$:Cr$^{3+}$, Wenger
and Güdel [23] for CsNaScCl₆:Cr³⁺, Avram and Brik [24] for LiCaAlF₆:Cr³⁺, Ring-Ling Chien et al. [15] for Cs₂GeF₆:Mn⁴⁺. All these authors analyzed the Ham reduction [25] of spin-orbit splitting of the ⁴T₂₂g excited state of the above-mentioned 3d³ ions. Studies of the ⁴T₂₂g excited state geometry were made in [22, 23], resulting in the evaluation of the magnitudes of the ligands displacements and getting the potential energy surface cross-sections for the excited state. Avram et al. [26] have investigated the electron-phonon interaction in the CsCaF₃:V²⁺ laser crystal and the geometry of the [VF₆]⁴⁻ complex in the ⁴T₂₂g excited state of the V²⁺ ion.

The aim of this paper is a theoretical analysis of the ⁴T₂₂g excited state in Cs₂GeF₆:Mn⁴⁺ crystal, with the main attention being paid to the geometry of this electronic state, influenced by its coupling with the total symmetric a₁g and double degenerated e₉ normal vibrations of the [MnF₆]²⁻ complex due to the dynamic Jahn–Teller effect. Such an analysis permits to estimate the changes of the chemical bond lengths due to the combined effect of the a₁g and eₙ normal modes, plot the cross-sections of the potential energy surface as a function of the ionic displacements, and deduce the value of the Jahn–Teller stabilization energy. The results of this investigation are accurate because the [MnF₆]²⁻ octahedron does not share faces, edges or corners with neighboring octahedra and is, therefore, weakly coupled to the lattice with quite sharp spectral features [16]. That is why the cluster model of Sturge [27], which treats an impurity center as an isolated molecule, can be used.

2. Experimental Support

The basis of our theoretical analysis will be the experimental energy data obtained from the optical spectra of the Cs₂GeF₆ crystals doped with Mn⁴⁺ ions. For this reason we present briefly in this section the results of the spectroscopic studies of Mn⁴⁺ centers in octahedral sites in Cs₂GeF₆ crystal carried out by Helmholtz and Russo [14], Chien et al. [15] and Campochiaro et al. [16].

Cs₂GeF₆ crystallizes in the Fm3m – O h₅ (antifluorite) space group with the lattice constant a = 3.60 Å [13]. Each germanium ion occupies a position with O₉ site symmetry and is surrounded by six fluorines at 1.80 Å distance. The [MnF₆]²⁻ ion may be introduced as an impurity such one obtains the system Cs₂MnF₆, with the Mn – F distance equal 1.74 Å [14]. So, in this system, Mn⁴⁺ at Ge sites in Cs₂GeF₆ is octahedrally coordinated by F⁻ ions. The [MnF₆]²⁻ unit has eight nearest – neighbor Cs⁺ ions lying outward the octahedron faces and forming a cube. The weak coupling of the [MnF₆]²⁻ unit to the rest of the lattice is readily justified by the following features: the sharpness of the vibrational lines, the near absence of lines due to GeF₆²⁻ octahedra, the weakness of acoustic phonon bands, and the host independence of the spectra [15]. The Mn⁴⁺ ion has three 3d electrons in its ground state, and all its visible and near ultraviolet spectra are due to the d → d transitions, in an exact analogy to Cr³⁺ or V²⁺. The one-photon spectrum consists of a weak magnetic dipole and some magnetic dipole sidebands, but is dominated by spectra based on the three odd parity modes of the [MnF₆]²⁻ octahedron [14]. In [14] the ⁴A₂g → ⁴T₂₂g transition has been investigated by one photon spectroscopy, and it was shown that the ⁴T₂₂g state undergoes spin-orbit splitting into I₁g, I₂g, I₂s components, in the order of increasing energy. The first three were identified at 20620.5, 20626.6 and 20636.5 cm⁻¹, with energies relative to that for the I₁g state having the values 0, 6.1, and 16 cm⁻¹ respectively.

The two photon spectra of Cs₂MF₆:Mn⁴⁺ have been observed by Chien et al. [15]. They have established the following fine structure of the ⁴T₂₂g excited state: I₁g : 0, I₂g : 102, I₂s : 54 and I₂a : 64 cm⁻¹ (all above 20625.8 cm⁻¹). An analysis of the Ham quenching for the ⁴A₂g → ⁴T₂₂g zero phonon line had also been made.

Campochiaro et al. [16] reported the low temperature (7 K) single crystal two photon spectra of the ⁴A₂g → ⁴T₂₂g transition in the Cs₂GeF₆:Mn⁴⁺. They observed all four zero-phonon lines of the ⁴A₂g → ⁴T₂₂g transition, and the multiplet components are assigned as I₁g at 0 cm⁻¹, I₂g at 11 cm⁻¹, I₂s at 64 cm⁻¹ and I₂a at 74 cm⁻¹. They pointed out that the line at 54 cm⁻¹ (assigned in [15] to I₂s) is actually a lattice mode, not a quartet component.

3. The ⁴A₂g → ⁴T₂₂g Transition in a Static Crystal Field

The absorption zero-phonon line for the above transition in the Cs₂GeF₆:Mn⁴⁺ crystal exhibits a fine structure resulting in four lines which correspond to the spin-orbit splitting of the ⁴T₂₂g level. The 12-fold-degenerated ⁴T₂₂g term is split by the spin-orbit interaction into four terms transforming as I₁g, I₂g, I₂s, I₂a irre-
ducible representations of the octahedral double group

\[ ^4T_{2g} \rightarrow \Gamma_5 + \Gamma_7 + \Gamma_8^a + \Gamma_8^b. \]

The full \( d^3 \) matrices of Eisenstein [28], including the spin-orbit interaction (\( \xi_{SO} = 380 \text{ cm}^{-1} \) for \( \text{Mn}^{4+} \) [29]) were used to calculate the energies of the four \( ^4T_{2g} \) spinors in a perfect octahedral static crystal field. The values \( Dq = 2063 \text{ cm}^{-1}, B = 491 \text{ cm}^{-1}, C = 4053 \text{ cm}^{-1} \) and \( \xi_{SO} = 380 \text{ cm}^{-1} \) are chosen to fit the absorption spectra of the title system from paper [15]. The results are shown in Table 1, column a. A comparison with the experimentally observed relative energies [16]. c) Calculation including the Jahn–Teller reduction parameter \( \gamma = 0.26 \).

The first three terms in (2) represent the Hamiltonians for free ion, crystal field and spin-orbit interactions, respectively. The last term represents the effective Hamiltonian which describes the interaction of the Mn\(^{4+}\) \( d^3 \) electrons with the lattice normal modes of the host crystal.

In the cluster model [27] we will consider the \([\text{MnF}_6]^{2-}\) octahedron as a cluster with the \( a_{1g}, e_g, t_{2g} \) Jahn–Teller active normal modes. In order to evaluate the constants of the vibronic coupling between these normal modes and the \( ^4T_{2g} \) electronic state we use the dynamic ligand field model [31, 32]. In the linear approximation of this model the vibronic coupling constants have the following explicit expressions [32]:

\[
\left\langle ^4T_{2g} \left\| \frac{\partial V}{\partial Q_{1g}} \right\| ^4T_{2g} \right\rangle = \frac{50}{\sqrt{6}} \frac{Dq}{R_0}, \tag{3}
\]

\[
\left\langle ^4T_{2g} \left\| \frac{\partial V}{\partial Q_{eg}} \right\| ^4T_{2g} \right\rangle = \frac{25}{\sqrt{3}} \frac{Dq}{R_0}, \tag{4}
\]

\[
\left\langle ^4T_{2g} \left\| \frac{\partial V}{Q_{t2g}} \right\| ^4T_{2g} \right\rangle = \frac{4\sqrt{3}}{7} \frac{Dq}{R_0} \left( \frac{5}{3} - \frac{3}{\eta} \right), \tag{5}
\]

where \( Dq = 2063 \text{ cm}^{-1} \) is the crystal field strength, \( R_0 = 1.74 \text{ Å} \) is the equilibrium distance between central ion and ligands, and the parameter \( \eta \) is

\[
\eta = \frac{\langle r^4 \rangle}{\langle r^2 \rangle} R_0^2. \tag{6}
\]

Here \( \langle r^4 \rangle \) and \( \langle r^2 \rangle \) are the averaged values of the corresponding power of the Mn\(^{4+}\) ion electron radial coordinate. This parameter is related to the well known angular overlap model (AOM) parameters \( e_{\sigma} \) and \( e_{\pi} \) [33] (\( e_{\delta} \equiv 0 \)):

\[
\eta = \frac{3}{5} \frac{3 - 4e_{\delta} / e_{\sigma}}{1 + e_{\delta} / e_{\sigma}}. \tag{7}
\]

From a two-dimensional spectrochemical series [34] the ratio of the AOM-parameters \( e_{\delta} \) and \( e_{\sigma} \) for \([\text{MnF}_6]^{2-}\) is obtained: \( e_{\sigma} / e_{\pi} \approx 0.31 \), and with (7), \( \eta \approx 0.8 \). Using the values of \( Dq, R_0 \) and \( \eta \), we obtain from (3), (4) and (5)

\[
\left\langle ^4T_{2g} \left\| \frac{\partial V}{\partial Q_{1g}} \right\| ^4T_{2g} \right\rangle = -0.48 \cdot 10^{-9} \text{N},
\]

\[
\left\langle ^4T_{2g} \left\| \frac{\partial V}{\partial Q_{eg}} \right\| ^4T_{2g} \right\rangle = -0.33 \cdot 10^{-8} \text{N},
\]
and 
\[
\left\langle 4T_{2g} \right| \frac{\partial V}{\partial Q_{3g}} \left| 4T_{2g} \right\rangle = -0.48 \cdot 10^{-9} \text{N}.
\]

As can be seen, the coupling to the t\(_{2g}\) mode is weaker than to the a\(_{1g}\) and e\(_{g}\) modes, and the excited state potential energy surface is shifted along the a\(_{1g}\) as well as e\(_{g}\) coordinates, the former being somewhat stronger than the latter. Even if the t\(_{2g}\)-coupling is smaller, the e\(_{g}\) vibronic coupling only with the 4T\(_{2g}\) electronic state of the Mn\(_{4}\)\([\text{MnF}_6]^{2-}\) cluster will distort only in the tetragonal direction. Taking this conclusion into account, in the next section, dedicated to the geometry of the excited state 4T\(_{2g}\) of Cs\(_2\)GeF\(_6\):Mn\(_{4}^{4+}\), we will treat the influence of the a\(_{1g}\) and e\(_{g}\) normal modes, and possibly a\(_{1g}\) with the most intense feature. That is why we will consider the linear 4\(T \otimes (e_g + t_{2g})\) coupling case, where the absolute e\(_{g}\) – minima coexist with t\(_{2g}\) – saddle points.

According to Wissing and Degen [32], in the title case \(\eta > 0.7\) and \(\nu_{eg}/\nu_{eg} > 0.5\) \((\nu_{eg} = 266 \text{ cm}^{-1}\) and \(\nu_{eg} = 494 \text{ cm}^{-1}\) \([14]\) the 4T\(_{2g}\) \(\otimes e_g\) minima are deeper than the 4T\(_{2g}\) \(\otimes t_{2g}\) minima, and the cluster [MnF\(_6\)]\(^{2-}\) distorts only in the tetragonal direction. Taking this conclusion into account, in the next section, dedicated to the geometry of the excited state 4T\(_{2g}\) of Cs\(_2\)GeF\(_6\):Mn\(_{4}^{4+}\), we will treat the influence of the a\(_{1g}\) and e\(_{g}\) vibronic coupling only with the 4T\(_{2g}\) electronic state of Mn\(_{4}^{4+}\) ions.

Using Avram and Brik’s analysis \([19, 35]\) of the Ham quenching of the origin multiplet, we obtain the values in column c of Table 1 (Sect. III) and calculate the Jahn–Teller stabilization energy in the 4T\(_{2g}\) state, \(E_{JT} = 438 \text{ cm}^{-1}\). It corresponds to the Jahn–Teller reduction parameter \(\lambda = \exp \left( -\frac{3}{2} \frac{E_{JT}}{\nu_{eg}} \right) = 0.26\) and a Huang–Rhys factor \(S_{eg} = 0.89\).

5. Geometry of the 4T\(_{2g}\) Excited State in Cs\(_2\)GeF\(_6\):Mn\(_{4}^{4+}\)

The adiabatic potentials corresponding to the ground and excited states of Mn\(_{4}^{4+}\) ions in the [MnF\(_6\)]\(^{2-}\) cluster have different geometries. This leads to a relative displacement of their potential energy surface along the a\(_{1g}\) and e\(_{g}\) normal modes of the cluster, as we have carried out in the end of last section.

In order to calculate the equilibrium displacements of the 4T\(_{2g}\) from the ground state along the a\(_{1g}\) and e\(_{g}\) active modes we use the following equation \([36]\)

\[
|\Delta Q_{i}|_{eq} = \left( \frac{2S_i\hbar\nu_i}{f_i} \right)^{1/2}.
\] (8)

The \(f_i\) constants were calculated with the FG matrix method for an octahedral [MnF\(_6\)]\(^{2-}\) cluster \([37]\). With \(h\nu_{a1g} = 512 \text{ cm}^{-1}\) and \(h\nu_{eg} = 494 \text{ cm}^{-1}\) \([13, 14]\), we obtain \(f_{a1g} = 218 \text{ N/m}\) and \(f_{eg} = 203 \text{ N/m}\), respectively.

The Huang–Rhys factor \(S_{eg} = 0.89\) was calculated at the end of the last section, based on the Ham quenching of the 4T\(_{2g}\) spin-orbit splitting due to the dynamical Jahn–Teller effect. The Huang–Rhys factor for vibronic coupling with the normal mode a\(_{1g}\) is \(S_{a1g} = 2.75\) \([38]\).

Using these data, we got, from (8), \(|\Delta Q_{a1g}|_{eq} = 0.16 \text{ Å}\) and \(|\Delta Q_{eg}|_{eq} = 0.09 \text{ Å}\). As previously demonstrated, based on group theoretical considerations and the 4T\(_{2g}\) wave functions \([39, 40]\), the sign of \(\Delta Q_{a1g}^{eq}\) is positive, whereas the sign of \(\Delta Q_{eg}^{eq}\) is negative.

Like in \([35]\), the coordinate system in the \((Q_{a1g}, Q_{eg})\) space can always be chosen in such a way, that the potential minimum of the 4T\(_{2g}\) component under consideration (either \(\xi\), \(\eta\) or \(\zeta\)) lies on the \(Q_{a1g}\) axis, i.e. no distortion occurs along \(Q_{eg}\). Then it is possible to consider the \(|\Delta Q_{a1g}^{eq}|_{eq}\) values as corresponding to \(|\Delta Q_{eg}^{eq}|_{eq}\), whereas \(|\Delta Q_{a1g}^{eq}|_{eq}\) is zero. Also, we will use the connection between displacements of normal coordinates
Fig. 2. Contour plot of the harmonic $^4T_{2g}$ potential energy surface for the Cs$_2$GeF$_6$:Mn$^{4+}$ system as a function of changes in the Mn$^{4+}$ – F$^-$ (x, y) and Mn$^{4+}$ – F$^-$ (z) chemical bond lengths. The energies of individual contours are given in hundreds of wave numbers. The open circle around the origin corresponds to the equilibrium position of the ground $^4A_{2g}$ potential energy surface; the black square indicates the equilibrium position of the $^4T_{2g}$ potential energy surface shifted with respect to the ground state as a combined result of the $a_{1g}$ and $e_g$ normal vibrations. The black circle shows the hypothetical position of the $^4T_{2g}$ potential energy surface minimum if there were no $e_g$ normal vibration (i.e. in the absence of the Jahn–Teller distortion). The value on the potential energy surface of the $^4T_{2g}$ state at this point (between 400 and 500 cm$^{-1}$ in the figure) corresponds to the Jahn–Teller energy for the considered complex. Details of calculations are given in the text.

\[
\begin{pmatrix}
\Delta x \\
\Delta y \\
\Delta z
\end{pmatrix} = \frac{1}{2} \begin{pmatrix}
\sqrt{\frac{2}{3}} & -\sqrt{\frac{2}{3}} & -1 \\
\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & 1 \\
\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & 0
\end{pmatrix} \begin{pmatrix}
\Delta Q_{a_{1g}} \\
\Delta Q_{e_g} \\
\theta
\end{pmatrix}. \tag{9}
\]

Equation (9) explains why it is convenient to perform a specific rotation of the coordinate system in the $(Q_\theta, Q_\epsilon)$ space described above: if $|\Delta Q_{e_g}|_{eq} = 0$, then $\Delta x = \Delta y$, and the potential energy surface can be easily visualised. Table 2 contains the Huang–Rhys factors and the equilibrium geometries of the [MnF$_6$]$^{2-}$ octahedron in the $^4T_{2g}$ first quartet excited state relative to the $^4A_{2g}$ ground state in the Mn$^{4+}$ doped Cs$_2$GeF$_6$ crystal.

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

It should be pointed out, that similar analyses performed for the Cr$^{3+}$ ion in Cs$_2$NaYCl$_6$:Cr$^{3+}$ and Cs$_2$NaYBr$_6$:Cr$^{3+}$ [20, 22], Cs$_2$NaScCl$_6$:Cr$^{3+}$ [23] and CsCaF$_3$:V$^{2+}$ [35] have lead to a deformation of the opposite sign along the z-axis, namely, to a slight axial contraction, whereas for CsCaF$_3$:V$^{2+}$ [26] and Cs$_2$GeF$_6$:Mn$^{4+}$ we have a slight axial stretching. The criterion, which defines the contraction along the z-axis deformation, is

\[
|\Delta Q_{a_{1g}}|_{eq} < |\Delta Q_{e_g}|_{eq} \sqrt{2}. \tag{10}
\]
If the above condition is not obeyed, the complex will expand along the z-axis.

6. Conclusions

In this paper we have calculated the fine structure of the first excited quartet $^4T_{2g}$ of an Mn$^{4+}$ ion doped in a Cs$_2$GeF$_6$ crystal. A theoretical analysis of vibronic interaction, manifested as dynamical Jahn–Teller effect, between the $^4T_{2g}$ state and $a_{1g}$, $e_g$, and $t_{2g}$ normal modes of the host matrix, shows that the coupling $^4T_{2g} \otimes (e_g + t_{2g})$ distorts the complex only in the tetragonal direction, and the $^4T_{2g} \otimes e_g$ minima are deeper than the $^4T_{2g} \otimes t_{2g}$ minima. Our model calculations show that the excited state potential energy surface $^4T_{3g}$ is shifted along the $a_{1g}$ as well as $e_g$ coordinates, the former being somewhat stronger than the latter. The combined coupling of the $^4T_{2g}$ electronic state of the Mn$^{4+}$ ion to the $a_{1g}$ and $e_g$ normal modes gave a possibility for estimation of the equilibrium displacements of the ligands. It is shown that the net result of both vibrations is a net equatorial expansion and a slight axial stretching, opposite to the case of trivalent chromium ions in different hosts. The Jahn–Teller stabilization energy $E_{JT} = 439.6 \text{ cm}^{-1}$ has been estimated from the contour plot of the potential surface energy in the $^4T_{2g}$ electronic state (Fig. 2). This result agrees well with results obtained from the Ham theory for this case.

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