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JAHN - TELLER EFFECT IN FIRST EXCITED STATE OF Mn^{4+} DOPED IN Cs_2SiF_6 CRYSTAL

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Abstract
In this paper, we study the fine structure of $^4T_{2g}$ energy level of Mn^{4+} ions doped in Cs_2SiF_6 crystal, the energy splitting of the zero-phonon line of $^4T_{2g} - {}^4A_{2g}$ emission band and vibronic coupling of the d^3 electrons with local mode of crystal lattice. The Mn^{4+} substitutes the Si ion in Cs_2SiF_6 and occupies an octahedral site surrounded by six fluorine ions in high strengths crystal field. In order to obtain the energy of the spin–orbit components Γ_6, Γ_7, Γ_8^a, Γ_8^b of $^4T_{2g}$ state of Mn^{4+} we have diagonalzed the Eisenstein matrices using the parameters Dq, B, C, ξ of Mn^{4+} ions in O_h crystal field of host matrix. The dynamical Jahn-Teller effect in $^4T_{2g}$ state quenches the total splitting of $^4T_{2g}$ state by Ham effect as proven by experimental data. From the reduction of the zero- phonon line split up to values according with experimental data we have calculated the Ham reduction factor and calculated the Jahn-Teller stabilization energy.
Keywords: Cs_2SiF_6: Mn^{4+}, Spin–orbit interaction, Jahn–Teller effect, Ham effect.

1. Introduction

Experimental and theoretical results regarding the splitting of the first excited state ($^4T_{2g}$) of Mn^{4+} doped in Cs_2SiF_6 crystal are presented by Luis Seijo et al [1]. Using the crystal field theory they obtained theoretical values which reproduce the experimental data within about a factor of 3. In order to explain the differences between the theoretical and experimental data we will take into account the dynamical Jahn - Teller interaction by introducing the second order spin - orbit Hamiltonian. Ham reduction factor, Jahn - Teller stabilization energy and the energy of the four spinors of the $^4T_{2g}$ state are calculated.

2. Experimental data

Our theoretical analysis has as started point the experimental energy data obtained from the optical spectra of the Cs_2SiF_6 crystal, doped with Mn^{4+}ions. The results of the spectroscopic studies were carried out by Luis Seijo, Joila Barandiaran and Donald S. McClure [1].

Cs_2SiF_6 crystallizes in Fm3m - O_h^5 (antifluorite) space group. Each Si ion occupies a position with O_h site symmetry and is surrounded by six fluorines at 1.695 Å distance. The Mn^{4+} substitutes the Si ion in the crystal and so he lies at the center of an octahedral array of F^- ions at a distance of 1.74 Å. The $[MnF_6]^{2-}$ cluster has eight Cs^+ ions, as nearest - neighbor, lying outward from the octahedron faces and forming a cube. The $[MnF_6]^{2-}$ cluster is very weak coupled with the rest of the lattice, this being justified by the following features: the sharpness of the vibrational lines, the near absence of lines due to $[SiF_6]^{2-}$ octahedra, the weakness of acoustic phonon bands and the host independence of the spectra. The experimental data show that the first excited state $^4T_{2g}$ is split by spin - orbit interaction into Γ_7 Γ_8^b Γ_6 Γ_8^a components identified at 20614, 20626, 20678 and 20682 cm^{-1}. In [1] there are also given the calculated peak energies using standard crystal field theory, taking spin - orbit interaction into account. The calculations were based on the crystal field parameters: Dq=2162.6 cm^{-1}, B=500 cm^{-1} ,C=4042 cm^{-1} and ξ_{3d}=380cm^{-1}.The relative energies are 86, 275 and 277 respectively, all above 21473 cm^{-1}. The theoretical data reproduce the experimental data within about a factor of 3. The differences between the theoretical and experimental data are eliminated by taking into account the dynamic Jahn - Teller effect and the Ham quenching.

3. Energy level calculation in static crystal field

The 12 fold - degenerated $^4T_{2g}$ term is split by the spin - orbit interaction into four terms.

$$^4T_{2g} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8^a + \Gamma_8^b \qquad (1)$$

In order to calculate the energies of the four spinors, the full d^3 matrices of Eisenstein [2], including the spin – orbit interaction, were used. The results are presented in Table 1 (column a.), in comparison with the experimental splitting (in column b). The calculated splitting is about three times higher. This can be explained by the manifestation of the Jahn – Teller effect, which partially quenches the orbital angular momentum and reduces the total spin – orbit splitting. This is known as Ham effect. In order to model the observed spin - orbit splitting we used the second order spin - orbit Hamiltonian [3]

$$H_{SO}^{eff} = \lambda \vec{L}\vec{S} + k\left(\vec{L}\vec{S}\right)^2 + \rho\left(L_x^2 S_x^2 + L_y^2 S_y^2 + L_z^2 S_z^2\right) \qquad (2)$$

where λ, k and ρ are adjustable parameters. Their values were determined by fitting the eigenvalues of the H_{eff} matrix to the $^4T_{2g}$ spinor splitting calculated with the full d^3 matrices of Eisenstein(column a). Obtained values are: λ = 77.5 cm^{-1}, k = 10 cm^{-1} and ρ = -1 cm^{-1}.

Table 1. *Relative energy (cm^{-1}) of the four spin-orbit components of the $^4T_{2g}$ state in $Cs_2SiF_6:Mn^{4+}$*

Γ	a	b	c
Γ_7	0	0	0
Γ_8^a	67,5	4,72	12
Γ_6	273,7	74,89	68
Γ_8^b	269,6	59,9	64

4. Dynamical Jahn - Teller effect in $^4T_{2g}$ state.

The static crystal field does not explain the observed fine structure of the first excited state of Mn^{4+} in $[MnF_6]^{2-}$. Taking into account the dynamical Jahn - Teller effect, the Hamiltonian has an extra term, H_{JT}, in comparison with the ,Mn^{4+} in the static octahedral crystal field. $H = H_{FI} + H_{CF} + H_{SO} + H_{JT}$ (3)

The first three terms in equation (3) represent the Hamiltonian for free ion, crystal field, spin - orbit and Jahn - Teller interactions respectively. The last term represents the effective Hamiltonian which describes the interaction of the 3d electrons with the normal modes of the host crystal lattice. Using the cluster model it is demonstrated [4, 5]

$$\langle i, M_s, 0,0 | H_{eff} | j, M_s', 0,0 \rangle = \langle i, M_s | H_{eff} | j, M_s' \rangle [\delta_{ij} + \gamma(1 - \delta_{ij})] \quad (4)$$

where γ represents the Ham reduction factor given by the relation: $\gamma = e^{-\frac{\chi}{2}}$ (5)

In equation (5) χ is the Jahn - Teller interaction parameter. $\chi = \frac{3E_{JT}}{\hbar\omega}$ (6)

The observed experimental $^4T_{2g}$ spinor splitting can now be fitted with the H_{eff} matrix, including the Ham reduction factor γ, by keeping previously determined values of the parameters λ, k and ρ fixed and letting only γ vary. The results are given in Table I column c and in Fig. 1.

The theoretical and experimental data are fitting for γ = 0.28.

Using equation (6), taking $\hbar\omega$ = 497 cm^{-1} [1] and γ = 0.28 we obtained E_{JT} = 422 cm^{-1}.

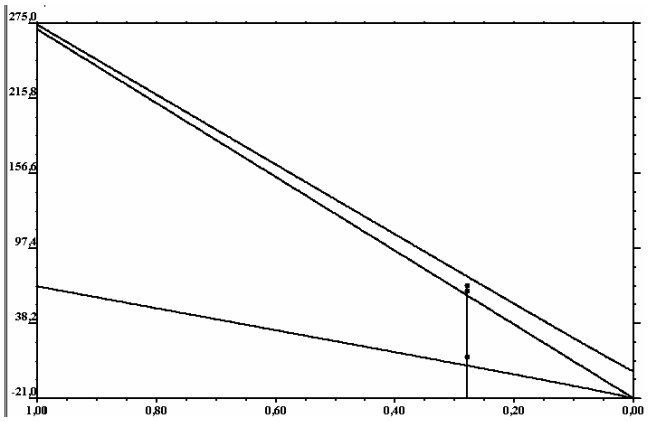

Fig. 1

5. Conclusions

Using the full d^3 matrices of Eisenstein the calculated relative energy of the four spinors of the first excited state $^4T_{2g}$ are: 86, 275 and 277 all above 21473 cm^{-1}. These values are overestimated by more than a factor of 3 in comparison with the experimental splitting. In order to model the observed spin - orbit splitting we used the second - order spin - orbit Hamiltonian and we determined the parameter λ, k and ρ which appear in this Hamiltonian. The values of this parameters: λ = 77.5 cm^{-1}, k = 10 cm^{-1} and ρ = -1 cm^{-1} were determined by fitting the eigenvalues of the H_{eff} matrix to the $^4T_{2g}$ spinors splitting values calculated with the full d^3 matrices of Eisenstein (column a). We represented the energies of the four spinors as functions of the Ham reduction factor γ and determined γ = 0.28, for which the theoretical and experimental data fit. The corresponding Jahn - Teller stabilization energy is E_{JT} = 422 cm^{-1}.

References

[1] L. Seijo, Z. Barandiaran, D.S. McClure, Int.J.Quant.Chem., **80**, 623 (200)

[2] J.C. Eisenstein, J. Chem. Phys., **34**, 1628 (1961).

[3] J. Kanamori, Progr.Theoret.Phys.(Kyoto) **17**, 177 (1957)

[4] F.S. Ham, Phys.Rev., **6A**, 1727 (1965).

[5] M.D. Sturge, Phys.Rev. B1, 1005 (1970)

[6] C. N. Avram, M. G. Brik, J. Lumin.,108, 319-322 (2004)

[7] N.M. Avram, M.G. Brik, Z.Naturforsch. 60a (1), pg. 54-60 (2005)