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HAM EFFECT IN THE $^4T_{1G}$ STATE OF Fe^{3+} DOPED IN $KMgF_3$

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Abstract. The aim of this paper is to investigate the Ham reduction of spin- orbit splitting of first excited state of iron doped $KMgF_3$:Fe^{3+} .In this crystal Fe^{3+} will substitute a Mg^{2+} ion and will be surrounded by six fluorine ions having a octahedral site symmetry. Using the parameters Dq, B, C and ξ of Fe^{3+} in an octahedral crystal field, we diagonalised the Eisenstein matrices and obtained the fine structure of the energy levels of ferric ion. The fine structure of the energy level $^4T_{1g}$ state ($\Gamma_6, \Gamma_7, \Gamma_8^a$ *and* Γ_8^b) is more larger than that experimental one due to Ham effect as result of Jahn-Teller interaction in first excited state of ferric ion doped in $KMgF_3$ crystal. We found the Ham quenching factor for which the theoretical and experimental data fit. Finally the ratio $E_{JT}/\hbar\omega$ was calculated and the results are discussed.
Key words: $KMgF_3$: Fe^{3+}, Eisenstein matrices, Ham quenching factor, dynamical Jahn Teller effect.

1. Introduction

$KMgF_3$, like other fluoride perovskites, was doped with different kind of 3d-ions in order to get tunable lasers in a large spectral domain: beginning with the infrared region and ending with the visible one. This large tunability region is due to the vibronic interaction between the optical electrons of the impurity ion and the vibration of the host lattice. This coupling can lead to non-radiative relaxation transitions and thus to the decrease of the laser efficiency. In order to reduce the non-radiative transitions it is recommendable to use crystals with relatively low cut-off phonon frequency [1]. The cut-off phonon frequency of the fluoride compounds is about 600 cm^{-1} so these crystals can be promising candidates for a solid state laser active media with weak non-radiative decay. A lot of spectroscopic studies were done on fluoride perovskites $KZnF_3$ and $KMgF_3$ doped with Cr^{3+} ion [2-8].

The spectroscopic properties of $KMgF_3$ doped with Fe^{3+} were studied by A. Poirier and D. Walsh [9]. Yu Wan Lun and Czeslaw Rudowicz [10] have calculated, using the crystal field theory, the spin orbit energies of $^4T_{1g}$ (P) state. The spacing of the splitting is 365 cm^{-1} in comparison with the experimental splitting spacing of 70 cm^{-1}[9].

In this paper we took into consideration the dynamical Jahn –Teller effect in $^4T_{1g}$ state which quenches the total splitting of the $^4T_{1g}$ state by Ham effect. By fitting the experimental

observed $^4T_{1g}$ spinor splitting with the calculated matrix elements of the second order spin-orbit Hamiltonian we obtained the Ham reduction factor γ and after that the ratio $E_{JT}/\hbar\omega$.

2. Crystal structure and spectroscopy of $KMgF_3:Fe^{3+}$

Our title host has a perovskite structure and belongs to the *Pm-3m* space group. The lattice constant is a = 3.9783 Å [11]. The impurity ion, Fe^{3+}, will be surrounding by six fluorine ions after substituting an Mg^{2+} ion. Because the electrical charge of the two ions are different, a charge compensating mechanism such as K^+ or Mg^{2+} vacancies is required. The site symmetry of the impurity ion can be non-distorted octahedral or two distorted octahedral (C_{3v} and C_{4v}). Because the non-distorted octahedral position is the most probable, in this paper we will study only this position.

Photoluminescence lines have been observed by A. Poirier and D. Walsh [9] for Fe^{3+} ions in $KMgF_3$ crystals at 14309, 14288, 14260 and 14239 (in cm^{-1}) due to the transitions between the first excited state ($^4T_{1g}$) and the ground state $^6A_{1g}$. Yu Wan Lun and Czeslaw Rudowicz [10] calculated the main parameters which determine the energy level scheme for any impurity ion in a host crystal, namely the crystal field strength Dq=1340cm^{-1} and the Racah parameters B=877.5cm^{-1} and C=3146.5cm^{-1}. The ratio Dq/B=1.52 which means that in this case the crystal field is weak.

The spin-orbit constant for the free Fe^{3+} ion is ξ_o = 486cm^{-1} [12] much larger than that of Fe^{3+} in the host crystal ξ=371cm^{-1}. The covalence reduction factor is 0.76.

3. Ham effect in the $^4T_{1g}$ state

The SO splitting of the $^4T_{1g}$ state calculated by Yu Wan Lun and Czeslaw Rudowicz in [10] is overestimated by a factor of 5, in comparison with the experimental data. This is due to the partial quenching of the total orbital momentum in the $^4T_{1g}$ state; therefore, a reduction of the total SO splitting appears.

In order to model the observed SO splitting we used the second order SO effective Hamiltonian [13 - 15].

$$H_{eff} = \lambda \vec{L} \cdot \vec{S} + k\left(\vec{L} \cdot \vec{S}\right)^2 + \rho\left(L_x^2 \cdot S_x^2 + L_y^2 \cdot S_y^2 + L_z^2 \cdot S_z^2\right) \qquad (1)$$

This Hamiltonian is defined in the space of the 12 wave functions of the $^4T_{1g}$ state with L = 1 and S = 3/2. The general form of these wave function is $|iM\rangle$ with the orbital function i transforming as the ξ, η and ζ orbital's [16] and M = -3/2, -1/2, 1/2, 3/2.

A diagonal matrix for the H_{eff} Hamiltonian can be obtaining by using symmetry-adapted wave functions:

$$\left|\Gamma\gamma\right\rangle = \sum_{i,M_s} C\left(i, M_s\right)\left|iM_s\right\rangle \tag{2}$$

where the coefficients C (i M_s) are taking from [17]. In this basis the eigenvalues can be expressed as a function of the parameters λ, k and ρ [18].

We determined the numerical values of the parameters that appear in equation (1) by fitting the eigenvalues of the H_{eff} to the calculated values of the $^4T_{1g}$ spinor splitting. The obtained values are λ=68cm^{-1}, k=-25 cm^{-1} and ρ=38cm^{-1}. Next we will take into account the interaction of the electronic $^4T_{1g}$ state with the e_g Jahn – Teller vibration active mode of the $[FeF_6]^{3-}$ octahedron.

Considering the effective Hamiltonian as a small perturbation in addition to the Jahn – Teller Hamiltonian, Sturge demonstrated [14] that the matrix elements of the effective Hamiltonian can be written as:

$$\left\langle Mi00\left|H_{eff}^{(I)}\right|M'j00\right\rangle = \left[\delta_{ij} + \gamma\left(1-\delta_{ij}\right)\right]\left\langle Mi\left|H_{eff}\right|M'j\right\rangle \tag{3}$$

Where $\gamma = e^{-\frac{3E_{JT}}{2\hbar\omega}}$, E_{JT} is the Jahn – Teller energy and ħω is the energy of the e_g Jahn – Teller active normal mode. Changing again the wave function into symmetry adapted basis, equation (3) transform into:

$$\left\langle\Gamma\gamma\left|H_{eff}^{(I)}\right|\Gamma\gamma\right\rangle = \sum_{i,M}\sum_{j,M'} C^*\left(i,M\right)\cdot C\left(j,M'\right)\cdot\left[\delta_{ij} + \gamma\left(1-\delta_{ij}\right)\right]\left\langle Mi\left|H_{eff}\right|M'j\right\rangle \tag{4}$$

Making the following substitutions: $\lambda \to \gamma\cdot\lambda, k \to \gamma\cdot k \; and \; \rho \to k + \rho - \gamma\cdot k$ in the first order perturbation theory, the eigenvalues of the H_{eff}^{I} will decrease exponentially, resulting an exponential decrease of the relative separation between the spinors.

In the second order perturbation theory following relation [14] gives the matrix elements of H_{eff}:

$$\left\langle\Gamma\gamma\left|H_{eff}^{(II)}\right|\Gamma\gamma\right\rangle = -\sum_{i,M}\sum_{j,M'} C^*\left(i,M\right)\cdot C\left(j,M'\right)\cdot\frac{\left[f_b\delta_{ij} + \left(1-\delta_{ij}\right)f_a\right]}{\hbar\omega}\times \times\sum_{l,M''}\left\langle Mi\left|H_{eff}\right|M''l\right\rangle\left\langle M''l\left|H_{eff}\right|M'j\right\rangle \tag{8}$$

$$f_a = e^{-x}\cdot G\left(\frac{x}{2}\right),\quad f_b = e^{-x}\cdot G\left(x\right),\quad G\left(x\right) = \int_0^x \frac{1}{u}\left(e^u - 1\right)du,\quad x = \frac{3E_{JT}}{\hbar\omega} \tag{9}$$

The last equations were used to calculate the eigenvalues of the effective Hamiltonian for γ varying from 0 to 1. We find out that for γ=0.22 the calculated eigenvalues fit to experimentally determined energies.

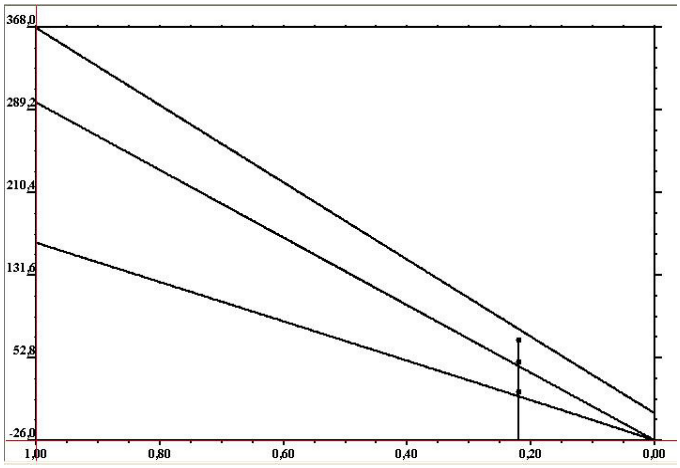

Fig.1. Dependence on γ of the four SO components.

For this value of γ we determined the energies of the four SO components given in Table 1. Next we calculated the ratio $E_{JT}/\hbar\omega=1.009$.

Table 1. *Comparison between the relative energies of the first excited state spinors.*

Oh double group irreducible representation	**A**	**b**	**c**
Γ_6	**0**	**0**	**0**
Γ_{8a}	**162**	**15**	**21**
Γ_{8b}	**296**	**43.2**	**49**
Γ_7	**366**	**78.3**	**70**

a. Calculated relative energies using the following parameters Dq=1340cm^{-1}, B=877.5cm^{-1} and C=3146.5cm^{-1}
b. Calculation including the Jahn – Teller effect with the Ham parameter γ=0.22
c. Experimentally observed energies.

4. Conclusions

As seen above the calculated values of the energies of the four spinors are overestimated by a factor of 5. In order to model the observed spin-orbit splitting we used the second order spin-orbit Hamiltonian. The values of the parameters λ, k and ρ, which appear in this Hamiltonian, for which the eigenvalues of H_{eff} matrix fit to the calculated values of the

$^4T_{1g}$ spinor splitting are: λ=68cm^{-1}, k=-25cm^{-1} and ρ=38cm^{-1}. Combining the Jahn-Teller and Ham effect, the spin-orbit splitting of $^4T_{1g}$ was reduced from 365cm^{-1} [11] to 78.3cm^{-1} ~ 70cm^{-1}, value which was obtained from the experimental data. These results were obtained for a Ham reduction factor of γ=0.22. The corresponding ratio $E_{JT}/\hbar\omega$=1.009.

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