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Jahn–Teller effect in the $^4T_{2g}$ excited state of Cr^{3+} ion in Cs_2NaYF_6 crystal

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Abstract

Calculations of the fine structure of Cr^{3+} energy levels in Cs_2NaYF_6 accompanied by estimations of the Jahn–Teller (JT) stabilization energy in the first excited $^4T_{2g}$ state of Cr^{3+} ion are presented. Two independent approaches—effective second-order spin–orbit Hamiltonian and analysis of the potential energy surfaces—are used. The JT energy was estimated to be 216 and 257 cm^{-1} in the first and the second models, respectively. It is shown that the octahedral $[CrF_6]^{3-}$ complex undergoes an equatorial expansion by 0.09 Å and an axial elongation by 0.02 Å due to the combined effect of the a_{1g} and e_g normal modes.
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Keywords: Jahn–Teller effect; Crystal field; Cr^{3+}-doped crystal

1. Introduction

Cubic elpasolite crystals doped with transition metal and rare earth ions have been extensively studied recently [1–4]. The chromium-doped elpasolite crystals are promising laser materials and serve as model systems for investigating crystal field and vibronic effects, because Cr^{3+} ions occupy practically perfect octahedral sites.

The present paper is aimed at calculating the fine structure of Cr^{3+} energy levels in Cs_2NaYF_6 and consideration of the dynamical Jahn–Teller (JT) effect in the $^4T_{2g}$ excited state. Effective second-order spin–orbit (SO) Hamiltonian is used to model the $^4T_{2g}$ state SO splitting, which is quenched due to the Ham effect [5] (from which the JT stabilization energy is estimated). Another approach consists in analysis of the potential energy surfaces shifts and combined effect of the a_{1g} and e_g normal modes of the octahedral complex. Both approaches (described in the next section) result in getting close values of the JT energy.

2. Ham reduction of the $^4T_{2g}$ state SO splitting

Calculations of the Cr^{3+} energy levels were performed in the cubic approximation using the following values of the crystal field strength D_q, Racah parameters B, C and SO constant (all in cm^{-1}): 1370, 754, 3393, and 224, respectively. Since, to the best of our knowledge, no absorption spectra for the Cs_2NaYF_6:Cr^{3+} system was published, the value of D_q was estimated from the results of the first-principles calculations [4,6]. Other parameters are typical for the Cr^{3+} ion in elpasolites [2]. Results of the energy calculations are shown in Table 1 (for the sake of brevity, only sublevels arising from the $^4T_{2g}$ state are given). The calculated SO splitting is more than two times greater than the observed one (Table 1). This is a manifestation of the dynamical JT effect in the $^4T_{2g}$ state of Cr^{3+}, which results in reduction of the magnitude of the SO splitting.

Using the Sturge method [7] and the second-order SO Hamiltonian we calculated the Ham reduction factor (which minimizes the discrepancies between the positions of the calculated and observed $^4T_{2g}$ components) $\gamma = \exp(-3E_{JT}/2\hbar\omega_e) = 0.447$ (with the energy of the e_g mode 402 cm^{-1} [1]). This allows for an immediate estimation of

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Table 1
Relative energies (in cm^{-1}) of four spin–orbit components of the $^4T_{2g}$ state in Cs_2NaYF_6:Cr^{3+}

Γ	a	b	c
Γ_7	0	0	0
Γ_8^a	46	17	21
Γ_8^b	106	45	47
Γ_6	141	66	63

(a) Calculation in static crystal field.
(b) Experimentally observed relative energies [1].
(c) Calculation including the Ham reduction parameter $\gamma = 0.447$ (this work).

Fig. 1. Contour plot of the harmonic $^4T_{2g}$ potential energy surface for Cs_2NaYF_6:Cr^{3+} as a function of changes in Cr^{3+}–F^-. The x-axis corresponds to the equatorial distortions, and the z-axis to the axial. The energies of the individual contours are given in hundreds of wave numbers (100, 200,…). 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. Black circle shows the hypothetical position of the $^4T_{2g}$ potential minimum if there were no e_g vibrations. The value on the potential energy surface of the $^4T_{2g}$ state at this point (around 257 cm^{-1}) corresponds to the JT stabilization energy for the considered complex.

the JT energy as 216 cm^{-1}, which is close to this value for other elpasolites [1].

3. Geometry of the $[CrF_6]^{3-}$ complex in the $^4T_{2g}$ electronic state

Due to the combined effect of lattice vibrations, the potential surface of the $^4T_{2g}$ excited state will split into three sheets, which will be displaced with respect to each other. Magnitudes of the normal mode displacements can be expressed in terms of the corresponding force constants, Huang–Rhys factors, and energies of the modes [8]. Following the line of our previous papers [4,9–11], with experimental data for the a_{1g} and e_g normal modes $\hbar\omega_{a_{1g}} = 501$ cm^{-1}, and $\hbar\omega_{e_g} = 402$ cm^{-1}, corresponding Huang–Rhys factors $S_{a_{1g}} = 3.20$, and $S_{e_g} = 0.64$ [1], we estimate the force constants $K_{a_{1g}} = 205$ N/m and $K_{e_g} = 132$ N/m, respectively. With these values the magnitudes $\left|\Delta Q_{a_{1g}}\right|_{eq}$, $\left|\Delta Q_{a_{1g}}\right|_{eq}$ of the a_{1g} and e_g modes are (in Å) 0.17 and 0.09, respectively, and the changes of the Cr–F distances are 0.097 (expansion in the xy plane) and 0.020 Å (axial stretching).

Finally, Fig. 1 shows a contour plot of the $^4T_{2g}$ potential surfaces. The equilibrium position of the ground state $^4A_{2g}$ is at the origin of the system of reference; the equilibrium position of the excited state is shown by the black square. Considering interaction with the a_{1g} normal mode (i.e. assuming $S_{e_g} = 0$) allows for estimating the values of the $\Delta x, \Delta y, \Delta z$ displacements produced by this fully symmetric vibtration only; they are $\Delta x = \Delta y = \Delta z = 0.07$ Å. This position is shown in Fig. 1 by the black circle. The co-ordinates of this point correspond to the co-ordinates of the point of intersection of three potential energy surfaces of the $^4T_{2g}$ electron state split by the e_g normal vibration. The value of the potential energy at this point (measured from the bottom of the potential energy surface) corresponds to the JT stabilization energy E_{JT}. The obtained value is $E_{JT} = 257$ cm^{-1}, which is very close to the one
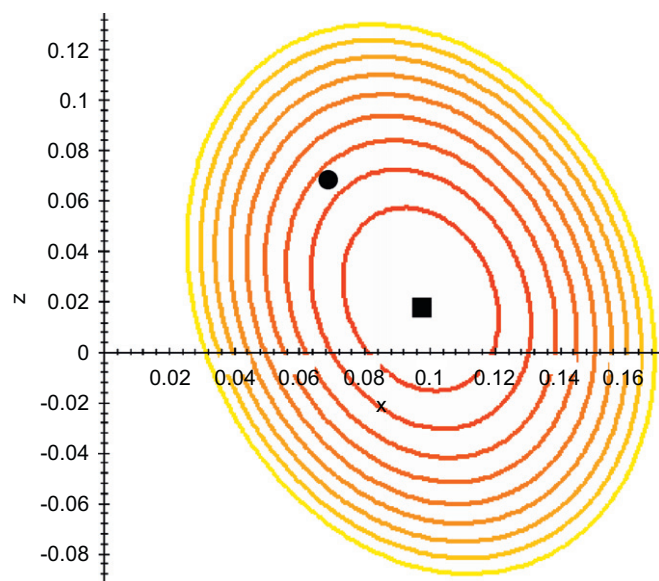
(255 cm^{-1}) reported in Ref. [1] from the analysis of the vibronic progressions.

4. Conclusions

Dynamical JT effect in the $^4T_{2g}$ state of Cr^{3+} in Cs_2NaYF_6 has been considered in the present paper. The value of the JT stabilization energy was calculated from both the Ham effect (216 cm^{-1}) and analysis of the excited state geometry (257 cm^{-1}). Distortions of the $[CrF_6]^{3-}$ complex were evaluated; it was shown that the complex expands both in the equatorial plane and along the z-axis. The results obtained in the present paper can be used for an analysis of the low-symmetry crystal field effects and their influence on the absorption spectrum of Cs_2NaYF_6:Cr^{3+}.

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