



Contents lists available at SciVerse ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

## Research on the optical spectra, $g$ factors and defect structures for two tetragonal $Y^{2+}$ centers in the irradiated $CaF_2: Y$ crystal

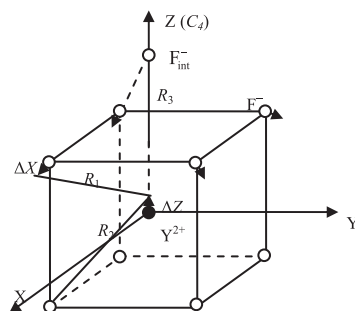
Wen-Chen Zheng<sup>a,c,\*</sup>, Yang Mei<sup>b,d</sup>, Yu-Guang Yang<sup>a</sup>, Hong-Gang Liu<sup>a</sup><sup>a</sup> Department of Material Science, Sichuan University, Chengdu 610064, PR China<sup>b</sup> School of Physics & Electronic Engineering, Mianyang Normal University, Mianyang 621000, PR China<sup>c</sup> International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, PR China<sup>d</sup> Research Center of Laser Fusion, CAEP, Mianyang 621000, PR China

### HIGHLIGHTS

- ▶ Optical and EPR spectra of two  $Y^{2+}$  centers in  $CaF_2$  are calculated.
- ▶ The calculations are from CDM and PTM methods.
- ▶ Calculated results from both methods show good agreement with observed values.
- ▶ The defect models and defect structures of both  $Y^{2+}$  centers are obtained.

### GRAPHICAL ABSTRACT

The optical and EPR data of two tetragonal  $Y^{2+}$  centers in  $CaF_2$  are calculated from two methods, CDM and PTM, the defect models of both  $Y^{2+}$  centers are confirmed and their defect structures are obtained.



### ARTICLE INFO

#### Article history:

Received 15 May 2012

Received in revised form 13 June 2012

Accepted 5 July 2012

Available online 16 July 2012

#### Keywords:

Electron paramagnetic resonance

Crystal-field theory

Defect structures

Optical spectroscopy

 $CaF_2$  $Y^{2+}$ 

### ABSTRACT

Based on the defect models that the tetragonal  $Y^{2+}$  (1) center in the irradiated  $CaF_2: Y$  crystal is due to  $Y^{2+}$  at  $Ca^{2+}$  site associated with a nearest interstitial  $F^-$  ion along  $C_4$  axis and the tetragonal  $Y^{2+}$  (2) center is  $Y^{2+}$  at  $Ca^{2+}$  site where the tetragonal distortion is caused by the static Jahn–Teller effect, the two optical spectral bands and anisotropic  $g$  factors for both tetragonal  $Y^{2+}$  centers are calculated. The calculations are made by using two methods based on the cluster approach, one is the complete diagonalization (of energy matrix) method (CDM) and another is the perturbation theory method (PTM). The calculated results for each  $Y^{2+}$  center from CDM and PTM coincide and show reasonable agreement with the experimental values. The calculated isotropic  $g$  factor for  $Y^{2+}$  (2) center at higher temperature owing to the dynamical Jahn–Teller effect is also consistent with the observed value. The defect structures (i.e., tetragonal distortion) of the two  $Y^{2+}$  centers are obtained from the calculation. It appears that both theoretical methods can be applied to explain the optical and EPR data, to study the defect model and to determine the defect structures for  $d^1$  ions in crystals.

© 2012 Elsevier B.V. All rights reserved.

### Introduction

Fluorite-type crystals  $MX_2$ , such as  $CaF_2$ , have been often employed as host lattices of transition metal and rare earth impurities

\* Corresponding author at: Department of Material Science, Sichuan University, Chengdu 610064, PR China.

E-mail address: [zhengwc1@163.com](mailto:zhengwc1@163.com) (W.-C. Zheng).

in order to acquire a detailed relationship among their optical and electron paramagnetic resonance (EPR) spectra and the defect model and defect structure of these impurity centers [1–7]. Importantly,  $MX_2$  doped with these impurity (particularly, the rare earth) ions can be used as solid state lasers, luminescence (including upconversion) materials and photovoltaic precursors [8–11]. Since these applications are connected to the defect model, defect structure and hence the spectroscopic properties of the impurity

centers, the optical and EPR spectra for transition metal and rare earth ions in  $MX_2$  crystals have been attracting significant interest [1–7,12–14]. Decades ago, the optical and EPR spectra for  $YF_3$  doped into  $CaF_2$  exposed to electron-radiation were measured [14]. It is found from the measurement that at low temperature ( $T \approx 4.2$  K) there are two tetragonal  $4d^1$   $Y^{2+}$  centers,  $Y^{2+}$  (1) and  $Y^{2+}$  (2), in the irradiated  $CaF_2$  crystal.  $Y^{2+}$  (1) center is assumed to  $Y^{3+}$  substituting for  $Ca^{2+}$ , the excess positive charge is compensated by a nearest interstitial  $F^-$  ion (called  $F_{int}^-$  in Fig. 1a) along  $C_4$  axis. When this material is exposed to electron-radiation,  $Y^{3+}$  ion traps an electron to become the tetragonal  $Y^{2+}$  (1) center [14]. In this center,  $Y^{2+}$  (1) ion should shift towards  $F_{int}^-$  ion by  $\Delta z$  and the four  $F^-$  ions between  $Y^{2+}$  (1) and  $F_{int}^-$  shift far away  $F_{int}^-$  by  $\Delta x$  because of the electrostatic interactions among them (see Fig. 1a). The defect structure (or tetragonal distortion) of  $Y^{2+}$  (1) center is therefore characterized by the shifts  $\Delta z$  and  $\Delta x$ . For  $Y^{2+}$  (2) center, the compensator  $F_{int}^-$  is remote (so,  $\Delta z = \Delta x = 0$ ) and the tetragonal distortion of  $(YF_8)^{6-}$  hexahedron is caused by the static Jahn–Teller effect, which lead the angle  $\theta$  (between metal–ligand distance and  $C_4$  axis) to differ from that ( $\theta_0 \approx 54.736^\circ$ ) in the cubic symmetry. The defect structure of  $Y^{2+}$  (2) center is characterized by angle  $\theta$ . The EPR  $g$  factors  $g_{||}$  and  $g_{\perp}$  at low temperature ( $T \approx 4.2$  K) and two optical spectra bands of both  $Y^{2+}$  centers and the isotropic  $g$  factor of  $Y^{2+}$  (2) center at higher temperature due to dynamical Jahn–Teller effect in  $CaF_2$  were obtained from EPR and optical spectra measurements [14]. So far no theoretical explanations for these EPR and optical spectral data concerning the above defect models for both  $Y^{2+}$  centers in  $CaF_2$  have been performed (in fact, few theoretical studies for the optical and EPR data of  $4d^1$  ions in 8-coordinated hexahedral clusters were reported). In order to confirm the defect models, to determine the defect structures and to explain reasonably these EPR and optical spectral data for  $Y^{2+}$  (1) and  $Y^{2+}$  (2) centers in  $CaF_2$ , in this paper, we calculated these spectroscopic data from two theoretical methods, namely the complete diagonalization (of energy matrix) method (CDM) and the perturbation theory method (PTM). Both methods are based on the cluster approach in which the one-electron basis functions are the molecular orbitals (MO) rather than the single d orbitals of central  $d^n$  ion (note: few theoretical studies based on the cluster approach for the optical and EPR data of  $4d^1$  ions in 8-coordinated hexahedral clusters were reported). The results are discussed.

## Calculation

In the cluster approach, the one-electron basis functions  $|\psi_\gamma\rangle$  (where  $\gamma = t$  or  $e$ , the irreducible representations of hexahedral  $O_h$  group) of a  $d^n$   $MX_8$  (or  $MX_4$ ) cluster can be expressed as [15,16]:

$$\begin{aligned}\psi_\gamma^Z &= N_\gamma^Z(|d_\gamma\rangle + \sqrt{3}\lambda_\beta^Z|\pi_\gamma\rangle) \\ \psi_\gamma^X &= N_\gamma^X(|d_\gamma\rangle + \lambda_\beta^X|\sigma_\gamma\rangle + \lambda_\beta^Y|\pi_\gamma\rangle)\end{aligned}\quad (1)$$

in which  $|d_\gamma\rangle$  is the d orbital of  $d^n$  ion, and  $|\sigma_\gamma\rangle$  and  $|\pi_\gamma\rangle$  are the p orbitals of ligand. The MO coefficients  $N_\gamma$  and  $\lambda_\beta$  ( $\beta = \sigma, \pi$ ) can be related by the normalization correlations,

$$\begin{aligned}N_e^Z &= [1 + 3(\lambda_\sigma^Z)^2 + 6\lambda_\pi^Z S_{dp}(\pi)]^{-1/2} \\ N_t^Z &= [1 + (\lambda_\sigma^Z)^2 + (\lambda_\pi^Z)^2 + 2\lambda_\sigma^Z S_{dp}(\sigma) + 2\lambda_\pi^Z S_{dp}(\pi)]^{-1/2}\end{aligned}\quad (2)$$

and the approximate relationships [15,16],

$$\begin{aligned}f_e &= (N_e^a)^4 [1 + 6\lambda_\pi^a S_{dp}(\pi) + 9(\lambda_\pi^a)^2 S_{dp}^2(\pi)] \\ f_t &= (N_t^a)^4 [1 + 2\lambda_\sigma^a S_{dp}(\sigma) + 2\lambda_\pi^a S_{dp}(\pi) + 2\lambda_\pi^a S_{dp}(\pi)\lambda_\sigma^a S_{dp}(\sigma) \\ &\quad + (\lambda_\sigma^a)^2 S_{dp}^2(\sigma) + (\lambda_\pi^a)^2 S_{dp}^2(\pi)]\end{aligned}\quad (3)$$

where  $f_\gamma \approx f_t \approx f_e$  is an adjustable parameter used to describe the covalence effects of  $MX_8$  cluster considered.

From Eq. (1), we have two spin–orbit parameters  $\zeta, \zeta'$  and two orbital reduction factors  $k, k'$  (where  $\zeta$  and  $k$  are caused by the interaction within  $t$  states, and  $\zeta'$  and  $k'$  are caused by that between  $t$  and  $e$  states), i.e., [15,16],

$$\begin{aligned}\zeta &= (N_t^a)^2 \left\{ \zeta_d^0 + \left[ \sqrt{2}\lambda_\pi^a \lambda_\sigma^a - (\lambda_t^a)^2 / 2 \right] \right\} \zeta_p^0 \\ \zeta' &= N_e^a N_t^a \left\{ \zeta_d^0 + \left[ \lambda_\pi^a \lambda_\sigma^a / \sqrt{2} + (\lambda_t^a)^2 / 2 \right] \right\} \zeta_p^0 \\ k &= (N_t^a)^2 \left[ 1 - (\lambda_\pi^a)^2 / 2 + \sqrt{2}\lambda_\pi^a \lambda_\sigma^a + 2\lambda_\sigma^a S_{dp}(\sigma) + 2\lambda_\pi^a S_{dp}(\pi) \right] \\ k' &= N_e^a N_t^a \left[ 1 + (\lambda_\pi^a)^2 / 2 + 4\lambda_\pi^a S_{dp}(\pi) + \lambda_\sigma^a S_{dp}(\sigma) + \lambda_\pi^a \lambda_\sigma^a / 2 \right]\end{aligned}\quad (4)$$

where  $\zeta_d^0$  and  $\zeta_p^0$  are the spin–orbit parameters of free  $d^n$  ion and free ligand ion, respectively. For  $CaF_2$ :  $Y^{2+}$  under study, we have  $\zeta_d^0(Y^{2+}) \approx 290$   $cm^{-1}$  [17] and  $\zeta_p^0(F^-) \approx 220$   $cm^{-1}$  [18].  $S_{dp}(\beta)$  are the group overlap integrals. They can be calculated from the Slater-type self-consistent field (SCF) functions [19,20]. For  $(YF_8)^{6-}$  cluster in  $CaF_2$ , we obtain  $S_{dp}(\pi) \approx 0.0018$  and  $S_{dp}(\sigma) \approx -0.0116$  from the above functions with the metal–ligand distance  $R_0 \approx 2.36$  Å [21] in  $CaF_2$ .

## Calculation using CDM

The Hamiltonian for a  $d^n$  ion in tetragonal crystal field and under an external magnetic field (note: the latter is required in EPR experiment) takes the form:

$$H = H_f + H_{CF}(Dq, Ds, Dt) + H_{SO}(\zeta, \zeta') + H_{Ze}(k, k'), \quad (5)$$

where the four terms are, respectively, the free-ion, the crystal-field, the spin–orbit and Zeeman (or magnetic) interaction terms

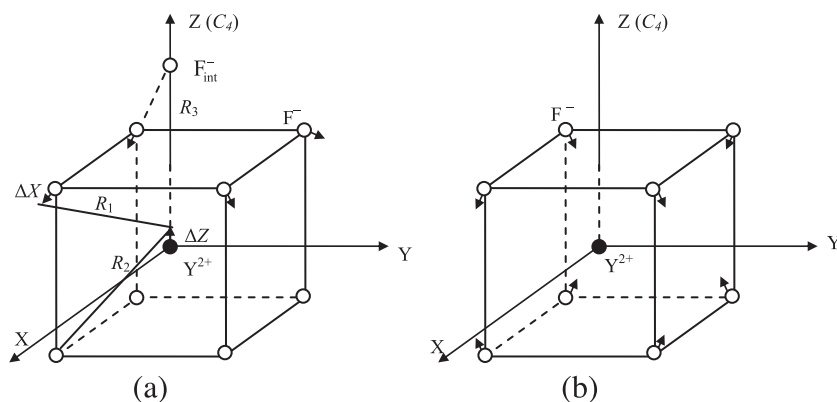


Fig. 1. The defect models of two tetragonal  $Y^{2+}$  centers in the irradiated  $CaF_2:Y$  crystal: (a)  $Y^{2+}$  (1) center, (b)  $Y^{2+}$  (2) center.

Download English Version:

<https://daneshyari.com/en/article/1232357>

Download Persian Version:

<https://daneshyari.com/article/1232357>

[Daneshyari.com](https://daneshyari.com)