Optik 164 (2018) 729–733

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Unified research of the EPR and optical spectral data for Cr^{3+}-doped $Lu_3Al_5O_{12}$ crystal

Xiao-Xuan Wu [a,*], Min Cheng [a], Wen-Chen Zheng [b], Bang-Xing Li [c]

[a] Department of Physics, Civil Aviation Flight University of China, Guanghan, 618307, PR China
[b] Department of Material Science, Sichuan University, Chengdu, 610064, PR China
[c] School of Science, Chongqing University of Technology, Chongqing, 400054, PR China

ARTICLE INFO

Article history:
Received 25 January 2018
Accepted 24 February 2018

Keywords:
Electron paramagnetic resonance
Optical spectrum
Crystal- and ligand-field theory
Cr^{3+}
$Lu_3Al_5O_{12}$

ABSTRACT

In this article, we apply a complete diagonalization (of energy matrix) method to simultaneously calculate the spin-Hamiltonian (or EPR) parameters (*g* factors $g_{//}$, $g_{\perp}$ and zero-field splitting *D*) and optical band positions (or crystal field energy levels) of Cr^{3+}-doped $Lu_3Al_5O_{12}$ (LuAG) crystal. The method is based on the two-spin-orbit-parameter model where besides the effects of spin-orbit parameter of central d^n ion in the common crystal-field theory, those of ligand ions are contained. The calculated results indicate that by using only three adjustable parameters, the eight observed spectroscopic data (three EPR data and five optical bands) are reasonably explained. This suggests that this diagonalization method is effective and applicable in the unified calculation of EPR and optical spectral data for d^3 ions in crystals. The local lattice distortion caused by the Cr^{3+} impurity in LuAG crystal is also estimated. The outcomes are discussed.

1. Introduction

Garnet crystals doped with transition-metal and rare-earth ions are the important laser materials [1–3]. Specially, the Cr^{3+}-doped garnet crystals can be applied in the fixed and adjustable frequency lasers [2,4–5]. So, knowledge of the spectroscopic properties of Cr^{3+}-doped garnet crystals is important to the development of effective laser devices and systems. Many spectroscopic experiments for Cr^{3+}-doped garnet crystals have been made [2–7]. For example, for Cr^{3+}-doped lutetium garnet $Lu_3Al_5O_{12}$ (LuAG) crystal, Markosyan et al. [6] measured its electron paramagnetic resonance (EPR) spectra and obtained the EPR (or spin-Hamiltonian) parameters $g_{//}$, $g_{\perp}$ and *D* decades ago. Burns et al [7] and Raudonyte et al. [8] carried out the optical spectral experiments and found five optical band positions (or crystal-field energy levels). Theoretically, however, up to date one cannot find the unified calculation or explanation for the eight observed spectroscopic data of LuAG: Cr^{3+} crystal in literature. It is known that the complete diagonalization (of energy matrix) method is a desirable and efficient approach to calculate simultaneously the EPR and optical spectral data [9,10]. Since the *g* factors, zero-field splitting *D* and first-excited state splitting $\Delta E(^2E)$ are closely connected with the spin-orbit parameter. The Hamiltonian of energy matrix should consist of the spin-orbit interaction. In the common crystal-field theory, only the effects due to spin-orbit parameter of central d^n ion are contained (i.e., the one-spin-orbit-parameter model) [4,9,10]. For completion and accuracy, in this article, we calculate simultaneously these EPR and optical spectral data for LuAG: Cr^{3+} crystal by means of the complete diagonalization method

* Corresponding author.
E-mail address: wxxdd@163.com (X.-X. Wu).

https://doi.org/10.1016/j.ijleo.2018.02.095
0030-4026/

based on the two-spin-orbit-parameter model where the effects of spin-orbit parameter of d^n ion and those of ligand ions are included [11]. Because these spectroscopic data of d^n impurity ion in crystals depend sensitively upon its immediate environment, the local lattice distortion caused by impurity is also estimated. The outcomes are discussed.

2. Calculation

In the two-spin-orbit-parameter model, the one-electron basis functions are required to include the *d*-orbitals of central d^n ion and *p*-orbitals of ligand ion. Consequently, we have two spin-orbit parameters ζ, ζ' and two orbit reduction factors k, k', i.e., [11]

$$\zeta = N_t(\zeta_d^0 + \frac{1}{2}\lambda_t^2\zeta_p^0),$$

$$\zeta' = (N_tN_e)^{\frac{1}{2}}(\zeta_d^0 - \frac{1}{2}\lambda_t\lambda_e\zeta_p^0)$$

$$k = N_t[1 - 2\lambda_t S_{dp}(t) + \frac{1}{2}\lambda_t^2],$$

$$k' = (N_tN_e)^{\frac{1}{2}}[1 - 2\lambda_t S_{dp}(t) - \lambda_e S_{dp}(e) - \frac{1}{2}\lambda_t\lambda_e] \quad (1)$$

where $\zeta_d{}^\circ$ and $\zeta_p{}^\circ$ represent the spin-orbit parameters of free d^n ion and free ligand ion. For the $(CrO_6)^{9-}$ cluster in LuAG:Cr^{3+} crystal under consideration, we find $\zeta_d{}^\circ(Cr^{3+}) \approx 273\,cm^{-1}$ [12] and $\zeta_p{}^\circ(O^{2-}) \approx 150\,cm^{-1}$ [13], $S_{dp}(\gamma)$ ($\gamma = t$ or e) denotes the group overlap integrals. They are commonly computed in terms of the Slater-type self-consistent field (SCF) functions [14,15] and the metal-ligand distance R. It is believed that the distance R in an impurity cluster in crystals is unlike the corresponding distance R_h in the host crystal because of the distinction between the ionic radius r_i of impurity and the r_h of the replaced host ion. People often estimate rationally the distance R for an impurity center in crystals by using the approximate equation $R = R_h + \frac{1}{2}(r_i - r_h)$ [16]. According to the values of $r_i(Cr^{3+}) \approx 0.63$ Å, r_h $(Al^{3+}) \approx 0.51$ Å [17] and $R_h \approx 1.939$ Å [18] of LuAG crystal, we obtain $R \approx 1.999$ Å for $(CrO_6)^{9-}$ clusters in LuAG:Cr^{3+} crystal. Based on the value of R, we get $S_{dp}(e) \approx 0.0896$ and $S_{dp}(t) \approx 0.0317$.

N_γ and λ_γ in Eq. (1) are the molecular orbital coefficients in the one-electron basis functions [19]. They can be evaluated by the normalization relationships [11,19]

$$N_\gamma\left[1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2\right] = 1 \quad (2)$$

and the approximate correlations

$$f_\gamma \approx \frac{B}{B_0} = \frac{C}{C_0} \approx N_\gamma^2\left[1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma)\right] \quad (3)$$

in which B and C are the Racah parameters for a d^n ion in crystals, and B_0 and C_0 are those for the free d^n ion. For free Cr^{3+} ion considered, we have $B_0 \approx 1030\,cm^{-1}$ and $C_0 \approx 3850\,cm^{-1}$ [12].

Cr^{3+} in LuAG crystal occupies the trigonal Al^{3+} octahedral site. Then, the Hamiltonian of a trigonal d^3 octahedral cluster in crystals based on the two-spin-orbit- parameter model is composed of the Coulomb, crystal-field and spin-orbit interaction terms, namely,

$$H = H_{Coul}(B, C) + H_{CF}(B_{20}, B_{40}, B_{43}) + H_{SO}(\zeta, \zeta') \quad (4)$$

where B_{kl} are the trigonal crystal-field parameters. The full energy matrix of the Hamiltonian is 120×120 dimensions and is fabricated with the aid of the strong field basis functions [20]. The eigenvalues of the energy matrix imply the crystal field energy levels and hence the optical band positions. The spin-Hamiltonian parameters can be computed by the eigenvalues $E(^4A_2, M_s)$ and eigenvectors $|^4A_2, M_s\rangle$ of the ground state $^4A_2$ by the formulas:

$$g_{//} = 2\left\langle \psi\left(^4A_2, \frac{1}{2}\right)\left|(k, k')L_z + g_eS_z\right|\psi\left(^4A_2, \frac{1}{2}\right)\right\rangle$$

$$g_\perp = \left\langle \psi\left(^4A_2, \frac{1}{2}\right)\left|(k, k')L_X + g_eS_X\right|\psi\left(^4A_2, -\frac{1}{2}\right)\right\rangle$$

$$D = \frac{1}{2}\left[E\left(^4A_2, \pm\frac{3}{2}\right) - E\left(^4A_2, \pm\frac{1}{2}\right)\right] \quad (5)$$

where g_e ($\approx$2.0023) is the g value of free ion. Thus, the EPR and optical spectral data can be acquired together by the complete diagonalization (of energy matrix) method.