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Investigations of the optical and EPR data and local structure for the trigonal tetrahedral Co^{2+} centers in $LiGa_5O_8$: Co^{2+} crystal

Jian He [a], Bi-Tao Liao [a], Yang Mei [a,*], Hong-Gang Liu [b], Wen-Chen Zheng [b]

[a] School of Mathematics & Physics, Mianyang Teachers' College, Mianyang, 621000, PR China
[b] Department of Material Science, Sichuan University, Chengdu, 610064, PR China

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ABSTRACT

In this paper, we calculate uniformly the optical and EPR data for Co^{2+} ion at the trigonal tetrahedral Ga^{3+} site in $LiGa_5O_8$ crystal from the complete diagonalization (of energy matrix) method founded on the two-spin-orbit-parameter model, where the contributions to the spectroscopic data from both the spin-orbit parameter of d^n ion (in the classical crystal field theory) and that of ligand ions are contained. The calculated ten spectroscopic data (seven optical bands and three spin-Hamiltonian parameters $g_{//}$, $g_\perp$ and D) with only four adjustable parameters are in good agreement with the available observed values. Compared with the host $(GaO_4)^{5-}$ cluster, the great angular distortion and hence the great trigonal distortion of $(CoO_4)^{6-}$ impurity center obtained from the calculations are referred to the large charge and size mismatch substitution. This explains reasonably the observed great g-anisotropy Δg $(= g_{//} - g_\perp)$ and zero-field splitting D for the $(CoO_4)^{6-}$ cluster in $LiGa_5O_8$: Co^{2+} crystal.

1. Introduction

$LiGa_5O_8$ is a well-known inverse spinel where Ga^{3+} ions occupy both the tetrahedral and octahedral sites and so there are three cationic sites, the trigonal tetrahedral Ga^{3+} site, the rhombic octahedral Ga^{3+} site and the trigonal octahedral Li^+ site in $LiGa_5O_8$ crystal [1] (see Fig. 1(a)). Co^{2+} ions doped into $LiGa_5O_8$ crystal can occupy the three cationic sites [2]. Among them, the tetrahedral Co^{2+} clusters in $LiGa_5O_8$: Co^{2+} have triggered considerable interest because the crystals including the tetrahedral Co^{2+} clusters can be used as the tunable laser materials in near-infrared region, the spectral hole-burning materials, and the saturable absorber in passive Q switch [3–8]. So, the optical and electron paramagnetic resonance (EPR) spectral experiments for Co^{2+} ions occupying the tetrahedral Ga^{3+} sites (to form the $(CoO_4)^{6-}$ centers) in $LiGa_5O_8$ crystals were carried out by some researchers [2,4,9–11]. These experimental studies found seven optical bond positions (or crystal-field energy levels) and three spin-Hamiltonian (or EPR) parameters (g factors $g_{//}$, $g_\perp$ and zero-field splitting D) for the tetrahedral $(CoO_4)^{6-}$ centers with trigonal symmetry in $LiGa_5O_8$ crystals [2,9–11]. Although the theoretical investigations for these spectroscopic data are of significance from the scientific and applied view of points, unfortunately, up to the present, there has no theoretical calculation, in particular, the unified theoretical calculation for all these spectroscopic data. The object of this study is to make a unified calculation for the optical and EPR spectral data for the trigonal $(CoO_4)^{6-}$ tetrahedral clusters in $LiGa_5O_8$ crystal from the complete diagonalization (of energy matrix) method on account of the two-spin-orbit-parameter model. In the model [12,13], for completion, besides the contributions from the spin-orbit parameter of central d^n ion in the classical crystal-field theory, the contributions from that of ligand ions via covalence effect are also contained. The defect structure of $(CoO_4)^{6-}$ tetrahedral clusters in $LiGa_5O_8$: Co^{2+} is also evaluated on the basis of the calculations. The results are discussed.

2. Calculation

The two-spin-orbit-parameter model for a d^n tetrahedral cluster in crystals demands the one-electron basis functions to change from the pure d orbitals of d^n ion in the conventional crystal-field theory to the molecular orbitals (MO) made up of the d oritals of d^n ion and the p orbitals of ligand ions, which results in two spin-orbit parameters ζ, ζ' and two orbit reduction factor k, k' [12,13]

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* Corresponding author.
E-mail address: pumermei@163.com (Y. Mei).

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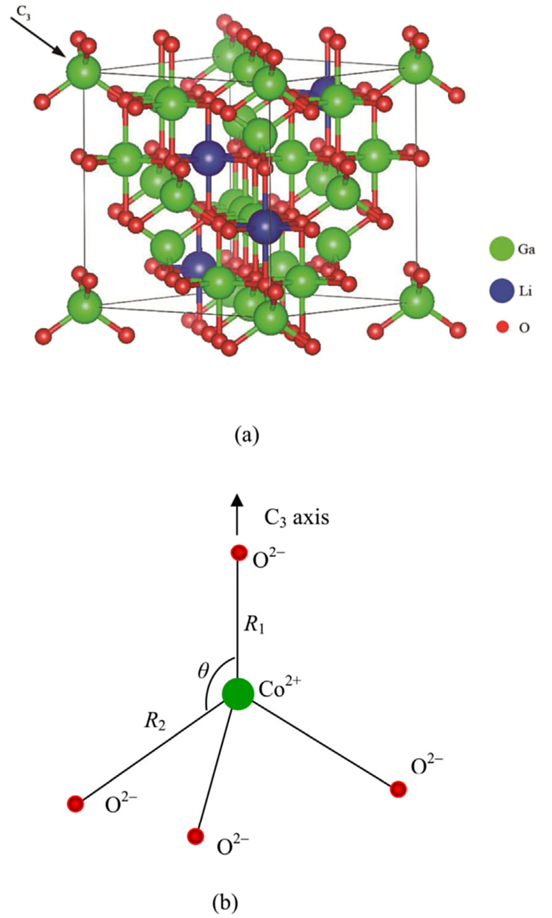

Fig. 1. (a) The structure of $LiGa_5O_8$ crystal, the tetrahedral Ga^{3+} site is at the vertex of cube. (b) The trigonal $(CoO_4)^{6-}$ tetrahedral cluster in $LiGa_5O_8{:}Co^{2+}$ crystal.

$$\begin{aligned}
\zeta &= N_t^2\left(\zeta_d^0+\left(\sqrt{2}\,\lambda_\pi\lambda_\sigma-\frac{(\lambda_\pi)^2}{2}\right)\zeta_p^0\right)\\
\zeta' &= N_tN_e\left(\zeta_d^0+\left(\frac{\lambda_\pi\lambda_\sigma}{\sqrt{2}}-\frac{(\lambda_\pi)^2}{2}\right)\zeta_p^0\right)\\
k &= N_t^2\left(1-\frac{(\lambda_\pi)^2}{2}+\sqrt{2}\,\lambda_\pi\lambda_\sigma+2\lambda_\pi S_{dp}(\pi)+2\lambda_\sigma S_{dp}(\sigma)\right)\\
k' &= N_tN_e\left(1+\frac{(\lambda_\pi)^2}{2}+\frac{\lambda_\pi\lambda_\sigma}{\sqrt{2}}+4\lambda_\pi S_{dp}(\pi)+\lambda_\sigma S_{dp}(\sigma)\right)
\end{aligned}\tag{1}$$

where N_γ ($\gamma = t$ or e) and λ_β ($\beta = \sigma$ or π) are the MO coefficients. ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit parameters of d^n ion and ligand ion in the free state. For $(CoO_4)^{6-}$ cluster considered, one can find ζ_d^0 $(Co^{2+}) \approx 533\ cm^{-1}$ [14], ζ_p^0 $(Co^{2+}) \approx 150\ cm^{-1}$ [15]. The group overlap integrals $S_{dp}(\sigma) = <d_t|\sigma_t>$ and $S_{dp}(\pi) = <d_t|\pi_t> = \langle d_e|\pi_e>/\sqrt{3}$ (where $|d_e>$ and $|d_t>$ stand for the d orbitals of $3d^n$ ion, and $|\pi_e>$, $|\pi_t>$ and $|\sigma_t>$ denote the p orbitals of ligand ions) depend upon the average metal-ligand distance R of the studied system. The difference of ionic radius r_i of impurity and the radius r_h of the replaced host ion can lead the distance R in an impurity center to differ from the corresponding distance R_h in the host crystal. We therefore employ an approximate equation $R = R_h + \frac{1}{2}(r_1 - r_2)$ [16] to evaluate the distance R. According to r_i $(Co^{2+}) \approx 0.72$ Å, r_h $(Ga^{3+}) \approx 0.62$ Å [17], R_{h1} $(Co^{2+}) \approx 1.882$ Å and R_{h2} $(Co^{2+}) \approx 1.876$ Å [1], we yield $R_1 \approx 1.932$ Å, $R_2 \approx 1.926$ Å (R_1 and R_2 are shown in Fig. 1 (b)) and so $\overline{R} \approx 1.928$ Å. So, the integrals $S_{dp}(\sigma) \approx -0.0376$ and $S_{dp}(\pi) \approx 0.0089$ are obtained from the Slater-type self-consistent field (SCF) functions with the distance $\overline{R}$ [18,19].

In the two-spin-orbit-parameter model, the Hamiltonian of a d^7 ion in the trigonal tetrahedron should take the form

$$H = H_{Coul.}(B,C) + H_{SO}(\zeta,\zeta') + H_{CF}(B_{20},B_{40},B_{43}) \tag{2}$$

in which the three terms denote, respectively, the Coulomb, spin-orbit and crystal field interactions. B and C are the Racah parameters in the system studied and B_{kl} are the crystal-field parameters in the Wybourne notation [20,21]. The optical bands can be given from the eigenvalues of the energy matrix of this Hamiltonian and the EPR parameters can be computed from the eigenvalues E $(^4A_2, M_s)$ and eigenvectors $|^4A_2, M_s\rangle$ of the ground state $^4A_2$ with the equations

$$\begin{aligned}
g_{//} &= 2\left\langle\psi\left(^4A_2,\frac{1}{2}\right)\middle|(k,k')L_Z+g_SS_Z\middle|\psi\left(^4A_2,-\frac{1}{2}\right)\right\rangle\\
g_\perp &= \left\langle\psi\left(^4A_2,\frac{1}{2}\right)\middle|(k,k')L_X+g_SS_X\middle|\psi\left(^4A_2,-\frac{1}{2}\right)\right\rangle\\
D &= \frac{1}{2}\left[E\left(^4A_2,\pm\frac{3}{2}\right)-E\left(^4A_2,\pm\frac{1}{2}\right)\right]
\end{aligned}\tag{3}$$

So, the optical and EPR data can be computed uniformly by the diagonalization of energy matrix method.

The complete energy matrix of the Hamiltonian is 120 × 120 and is constructed by virtue of the strong field basis functions [22]. In the energy matrix, the crystal field parameters B_{kl} are calculated using the empirical superposition model [23]. The effectiveness of this model in the analyses of crystal-field parameters has received the support from the exchange charge model [24,25] and the angular overlap model [23,26]. In the superposition model, the parameters B_{kl} for a trigonal tetrahedral cluster in crystals are expressed as

$$\begin{aligned}
B_{20} &= \overline{A}_2(R_0)\left[2\left(\frac{R_0}{R_1}\right)^{t_2}+3\left(\frac{R_0}{R_2}\right)^{t_2}(3\cos^2\theta-1)\right]\\
B_{40} &= \overline{A}_4(R_0)\left[8\left(\frac{R_0}{R_1}\right)^{t_4}+3\left(\frac{R_0}{R_2}\right)^{t_4}(35\cos^4\theta-30\cos^2\theta+3)\right]\\
B_{43} &= 6\sqrt{35}\overline{A}_4(R_0)\left(\frac{R_0}{R_2}\right)^{t_4}\sin^3\theta\cos\theta
\end{aligned}\tag{4}$$

where the power-low exponents $t_3 \approx 3$ and $t_5 \approx 5$ [12,13,27–29]. The reference distance $R_0 \approx \overline{R}$. The intrinsic parameter ratio $\overline{A}_2(R_0)/\overline{A}_4(R_0)$ for $3d^n$ ions in many crystals is found in the range of 8–12 [12,13,27–30]. Here the mean ratio $\overline{A}_2(R_0)/\overline{A}_4(R_0) \approx 10$ is applied. Angle θ is shown in Fig. 1(b). Analogous to the case of bond lengths R_i, the bond angle θ in an impurity center may not be like the corresponding angle θ_h in the host crystal because of the impurity-caused local lattice relaxation. Here we assume $\theta = \theta_h + \Delta\theta$, where $\theta_h \approx 109.55°$ [1] and $\Delta\theta$ refers to the impurity-caused angular distortion and is treated as an adjustable parameter.

The calculations of parameters ζ, ζ', k and k' in the energy matrix need the MO coefficients N_γ and λ_β. They can be estimated by means of the normalization correlations [12,13].

$$\begin{aligned}
&N_e^2\left[1+3\lambda_\pi^2+6\lambda_\pi S_{dp}(\pi)\right]=1\\
&N_t^2\left[1+\lambda_\sigma^2+\lambda_\pi^2+2\lambda_\sigma S_{dp}(\sigma)+2\lambda_\pi S_{dp}(\pi)\right]=1
\end{aligned}\tag{5}$$

and the approximate relationships

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

in which $f_t \approx f_e \approx f_\gamma \approx \frac{1}{2}(B/B_0 + C/C_0)$. The Racah parameters B_0 and C_0