

Researches of the optical band positions, spin-Hamiltonian parameters and defect structures for Cr³⁺-doped colquiriite-type fluoride crystals LiSrGaF₆, LiSrAlF₆ and LiCaAlF₆



Li-Rong Yang^a, Chen-Fu Wei^a, Yang Mei, Dr. Ph.D^{b,c,*}, Wen-Chen Zheng^d

^a School of Chemistry & Chemical Engineering, Mianyang Normal University, Mianyang 621000, PR China

^b School of Mechanical & Electrical Engineering, Mianyang Normal University, Mianyang 621000, PR China

^c Research Center of Computational Physics, Mianyang Normal University, Mianyang 621000, PR China

^d Department of Material Science, Sichuan University, Chengdu 610064, PR China

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ABSTRACT

The optical and EPR data of Cr³⁺-doped colquiriite-type fluoride crystals LiSrGaF₆, LiSrAlF₆ and LiCaAlF₆ are computed from the complete diagonalization of energy matrix method based on the two-spin-orbit-parameter model. This model takes account of the contributions due to both the spin-orbit parameter of central *dⁿ* ion (in the traditional crystal field theory) and that of ligand ions via covalent effect. The computed results indicate that the observed five optical band positions and three spin-Hamiltonian parameters (*g* factors *g_{||}*, *g_⊥* and zero-field splitting *D*) can be explained reasonably with only four adjustable parameters. The defect structures of Cr³⁺ centers in these crystals are also achieved from the calculations. It is suggested that the trigonal MF₆ octahedra in LiSrMF₆: Cr³⁺ (M = Al, Ga) crystals change from the compression (along C₃ axis) in the host crystals to the elongation in the Cr³⁺ impurity centers. The results are discussed.

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1. Introduction

Colquiriite-type fluorides LiBMF₆ (B and M denote a divalent and trivalent cations, respectively), such as LiSrGaF₆, LiSrAlF₆ and LiCaAlF₆, are the well-known tunable laser materials because they exhibit high intrinsic lasing efficiency and low thermal lensing [1–4]. Furthermore, they can be applied to build femtosecond lasers [5] and regenerative amplifiers [6]. So, considerable interest has been focused on the spectroscopic investigations of Cr³⁺-doped LiBMF₃ crystals [1,2,7–9] because these studies can provide some information on the electronic and spin energy levels and the defect structures of the studied crystals. The optical and electron paramagnetic resonance (EPR) spectra of Cr³⁺-doped LiSrGaF₆, LiSrAlF₆ and LiCaAlF₆ crystals were measured [1,2,7–9]. It is found from these measurements that Cr³⁺ ions occupy the trigonal M sites and undergo a weak octahedral crystal field. Five crystal field energy levels (or optical band positions) and three spin-Hamiltonian parameters (*g* factors *g_{||}*, *g_⊥* and zero-field splitting *D*) were also obtained from the spectroscopic experiments [1,2,7–9]. Up to now, no unified theoretical calculations for these spectroscopic

data have been reported. The aim of this paper is to calculate simultaneously these spectroscopic data from the complete diagonalization (of energy matrix) method based on the two-spin-orbit-parameter model. The model takes account of the contributions to the spectroscopic (especially, the EPR) data from both the spin-orbit parameter of central *dⁿ* ion (in the traditional crystal field theory) and that of ligands via covalent effect [10,11]. In view of the fact that the spectral data (particularly, the EPR data) depend sensitively upon the defect structure of *dⁿ* impurity center in crystals, the defect structures of Cr³⁺ centers in these LiBMF₆ crystals are also estimated. The results are discussed.

2. Calculation

The one-electron basis functions in the two-spin-orbit-parameter model are the linear combinations of *d* orbitals $|d_{\gamma}\rangle$ of *dⁿ* ions and *p* orbitals $|p_{\gamma}\rangle$ of ligands. These functions lead to two spin-orbit parameters ζ , ζ' and two orbit reduction factors *k*, *k'* [10,11]

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \frac{1}{2}\lambda_t^2\zeta_p^0), & \zeta' &= (N_tN_e)^{\frac{1}{2}}(\zeta_d^0 - \frac{1}{2}\lambda_t\lambda_e\zeta_p^0) \\ k &= N_t[1 - 2\lambda_tS_{dp}(t_{2g}) + \frac{1}{2}\lambda_t^2], & k' &= (N_tN_e)^{\frac{1}{2}}[1 - 2\lambda_tS_{dp}(t_{2g}) - \lambda_eS_{dp}(e_g) - \frac{1}{2}\lambda_t\lambda_e] \end{aligned} \quad (1)$$

* Corresponding author.

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

where N_γ ($\gamma = t$ or e , the irreducible representation of O_h group) and λ_γ (the orbital mixing coefficient) are the molecular orbital (MO) coefficients. ζ_d^0 and ζ_p^0 are the spin-orbit parameters of free d^n ion and ligand ion in the free state. For the LiBMF_6 : Cr^{3+} under study, we have ζ_d^0 (Cr^{3+}) $\approx 273 \text{ cm}^{-1}$ [12], ζ_p^0 (F^-) $\approx 220 \text{ cm}^{-1}$ [13]. The group overlap integrals $S_{dp}(\gamma)$ can be computed from the Slater-type self-consistent field (SCF) functions [14,15] and the metal-ligand distance R . The distance R in an impurity center is unlike that R_h in the host crystal because of the difference between the ionic radii r_i of impurity and r_h of the replaced host ion. We estimate the distance R from the approximate formula $R \approx R_h + \frac{1}{2}(r_i - r_h)$ [16] here. Thus, from the values of r_i (Cr^{3+}) $\approx 0.63 \text{ \AA}$, r_h (Ga^{3+}) $\approx 0.62 \text{ \AA}$, r_h (Al^{3+}) $\approx 0.51 \text{ \AA}$ [17] and the distances R_h for the three LiBMF_6 crystals (see Table 1), we yield the distances R for Cr^{3+} -doped LiBMF_6 crystals (see Table 1). The integrals $S_{dp}(\gamma)$ are therefore calculated and the results are listed in Table 1.

Thus, the Hamiltonian of a d^3 ion in trigonal crystal field in the two-spin-orbit-parameter model takes the form:

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

in which the three terms are Coulomb interaction, spin-orbit interaction and crystal field interaction terms. B_{kl} are the crystal field parameters in the Wybourne notation [20,21]. The crystal field energy levels and hence the optical band positions correspond to the eigenvalues of the energy matrix of the Hamiltonian in Eq. (2), and the spin-Hamiltonian parameters can be computed from the eigenfunctions ($^4A_2, M_s$) and eigenvalues $E(^4A_2, M_s)$ of the ground state 4A_2 by the following equations:

$$\begin{aligned} g_{//} &= 2 \langle ^4A_2, \frac{1}{2} | (k, k')L_z + g_e S_z | ^4A_2, -\frac{1}{2} \rangle \\ g_{\perp} &= \langle ^4A_2, \frac{1}{2} | (k, k')L_x + g_e S_x | ^4A_2, -\frac{1}{2} \rangle \\ D &= \frac{1}{2} \left[E \left(^4A_2, \pm \frac{3}{2} \right) - E \left(^4A_2, \pm \frac{1}{2} \right) \right] \end{aligned} \quad (3)$$

Thus, the optical and EPR data of Cr^{3+} in trigonal crystal field can be simultaneously calculated by using the diagonalization of energy matrix method.

We construct the 120×120 complete energy matrix of the above Hamiltonian in terms of the strong field basis functions [13]. In the matrix, the trigonal crystal field parameters B_{kl} are calculated by the following expressions obtained from the superposition model [22], i. e.,

$$\begin{aligned} B_{20} &= 6\bar{A}_2(R_0)(3\cos^2\theta - 1) \\ B_{40} &= 6\bar{A}_4(R_0)(35\cos^4\theta - 30\cos^2\theta + 3) \\ B_{43} &= -12\sqrt{35}\bar{A}_4(R_0)\sin^3\theta\cos\theta, \end{aligned} \quad (4)$$

where $\bar{A}_k(R_0)$ ($k=2, 4$) stand for the intrinsic parameters. Researches on the crystal field parameters in the optical and EPR spectra with the superposition model for $3d^n$ ions in many materials suggest that $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 8-12$ [11,23–27]. Here the average value $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 10$ is applied. θ is the angle between the direction of distance R and C_3 axis (see Fig. 1). Similar to the distance R , the angle θ in an impurity center may differ from the corresponding angle θ_h in the host crystal. Here we take $\theta \approx \theta_h + \Delta\theta$, where $\Delta\theta$, an adjustable parameter, represents the

Table 1
The structural data and group overlap integrals for Cr^{3+} -doped LiBMF_6 crystals.

	$R_h(\text{\AA})$	$R(\text{\AA})$	θ_h (deg.)	θ (deg.)	$S_{dp}(t)$	$S_{dp}(e)$
LiSrGaF_6 : Cr^{3+}	1.885 [18]	1.890	55.24 [18]	54.59	0.0315	0.0922
LiSrAlF_6 : Cr^{3+}	1.806 [19]	1.866	54.96 [19]	54.70	0.0344	0.0984
LiCaAlF_6 : Cr^{3+}	1.805 [19]	1.865	55.27 [19]	54.98	0.0345	0.0987

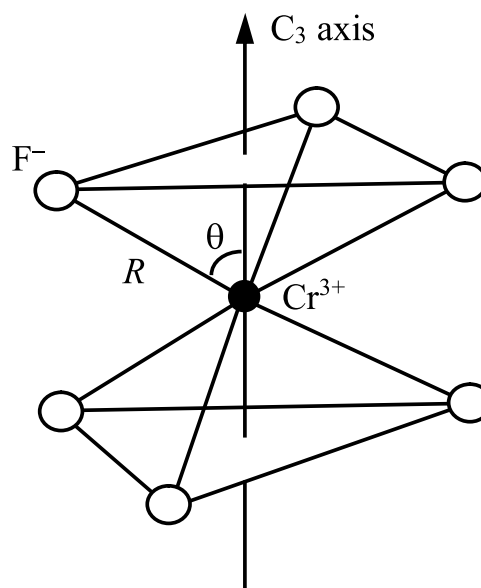


Fig. 1. The trigonal distortion of $(\text{CrF}_6)^{3-}$ octahedral clusters in LiBMF_6 crystals.

impurity-induced angular distortion of impurity center. The values of θ_h in the three host LiBMF_6 crystals are collected in Table 1.

For calculating the parameters ζ, ζ', k and k' in the energy matrix and Eq. (3), one should know the MO coefficients. These coefficients obey the normalization connections [11]

$$N_\gamma [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2] = 1 \quad (5)$$

and the approximate correlations [11]

$$f_\gamma = \frac{1}{2}(B/B_0 + C/C_0) = N_\gamma^2 [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma)] \quad (6)$$

in which B_0 ($\approx 1030 \text{ cm}^{-1}$ [12]) and C_0 ($\approx 3850 \text{ cm}^{-1}$ [12]) are the Racah parameters of free Cr^{3+} ion. The Racah parameters B and C for Cr^{3+} ion in the three ABMF_6 crystals are treated as the adjustable parameters. Thus, in the calculations, there are four adjustable parameters $B, C, \bar{A}_4(R_0)$ and $\Delta\theta$. The diagonalizing calculations find that for the three Cr^{3+} -doped LiBMF_6 crystals, when the four parameters take the values shown in Table 2, good agreements between the calculated and experimental optical and EPR data can be reached. The angles θ based on the impurity-induced angular distortions $\Delta\theta$ for the three Cr^{3+} -doped LiBMF_6 crystals are compared with the host angles θ_h in Table 1. The comparisons of optical and EPR data between calculation and experiment for the three Cr^{3+} -doped LiBMF_6 crystals are shown in Table 3 and Table 4, respectively.

3. Discussion

The nature (elongation or compression along C_3 axis) of a trigonal octahedral cluster depends upon the sign of $(\theta - \theta_0)$ (where $\theta_0 \approx 54.74^\circ$, the same angle in cubic octahedron). When $\theta - \theta_0 > 0$, the trigonal octahedron is compressed, whereas if

Table 2
The parameters used in calculations of the optical and EPR data for Cr^{3+} -doped LiBMF_6 crystals.

	B (cm^{-1})	C (cm^{-1})	$\bar{A}_4(R)$ (cm^{-1})	$\Delta\theta$ (deg.)
LiSrGaF_6 : Cr^{3+}	738	3400	1150	-0.65
LiSrAlF_6 : Cr^{3+}	744	3300	1180	-0.26
LiCaAlF_6 : Cr^{3+}	760	3200	1200	-0.29

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