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Studies of the g factors of the ground $^4A_2$ and the first excited ^2E state of Cr^{3+} ions in emerald

Qun Wei [a,*], Li-Xin Guo [a], Zi-Yuan Yang [b], Bing Wei [a]

[a] School of Science, Xidian University, Xi'an 710071, PR China
[b] Department of Physics, Baoji University of Arts and Science, Baoji 721007, PR China

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ABSTRACT

By using complete diagonalization method, the zero-field splitting and g factors of the ground $^4A_2$ and the first excited ^2E states of Cr^{3+} ions in emerald are calculated. The theoretical results are in good agreement with the experimental data. The dependencies of the g factors on the crystal field parameters, including Dq, v, and v', have been studied. It is shown that, the g factors of the ground state varied with the crystal field parameters approximately in a linear way, but the g factors of the first excited state varied nonlinearly with these parameters.

1. Introduction

Emerald ($Be_3Si_6Al_2O_{18}$:Cr^{3+}) is of great interest because of applications as the tunable solid-state laser material and has been studied experimentally and theoretically by many researchers [1–10]. The host $Be_3Si_6Al_2O_{18}$ crystal has the beryl structure with the space group designated as $P6/mcc$ and two molecules per unit cell. Cr^{3+} ions doped into $Be_3Si_6Al_2O_{18}$ crystals, substitute for the Al^{3+} ions with D_3 site symmetry. The six oxygen ligands around Cr^{3+} ions are located at the vertices of a slightly distorted octahedron having the [1 1 1] direction along the C_3 axis of the unit cell. The ground state of $Cr^{3+}(3d^3)$ ions at trigonal symmetry sites is $^4A_2(F)$, and the first excited state is $^2E(G)$. Yin et al. [1] confirmed there exist the Jahn–Teller effects in emerald by studying the optical spectra. Wood [9] and Fairbank et al. [2] reported the optical spectra and the zero-field splittings (ZFSs) of $^4A_2$ and ^2E states. Wang et al. [8] studied the local polarization phenomena of $(CrO_6)^{9-}$ cluster in emerald, and reported that oxygen ligands in $(CrO_6)^{9-}$ cluster exhibit remarkable polarization effect due to the effect of surrounding environment. Taking into account the spin–orbit interaction only, Macfarlane [10] calculated the ZFS and g factors of $^4A_2$ and ^2E states by using analytical and numerical methods. In the present work, by taking into account the spin–spin (SS), spin-other-orbit (SOO), and orbit–orbit (OO) interactions as well as the spin–orbit (SO) interaction, the ZFS and g factors of $^4A_2$ and ^2E states have been calculated. The theoretical results are in good agreement with the experimental data. The dependencies of the g factors on crystal field parameters have been studied.

2. Theory

The energy matrices for the $3d^3$ configuration ion in a crystal have been established using the Hamiltonian [11,12]

$$H = H_{ee}(B, C) + H_{CF}(B_{kq}) + H_M(\zeta, M_0, M_2) \quad (1)$$

where H_{ee}, H_{CF}, and H_M represent, respectively, the electrostatic, the crystal field (CF), and the magnetic interactions. H_{CF} in the Wybourne notation is given for trigonal symmetry type I (C_{3v}, D_3, D_{3d}) as [11,13–17]:

$$H_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{43}C_3^{(4)} + B_{4-3}C_{-3}^{(4)} \quad (2)$$

where B_{kq} are CF parameters with $B_{4-3} = -B_{43}$ for trigonal symmetry type I, and $C_q^{(k)}$ are normalized spherical harmonics. The CF parameters B_{kq} can be expressed in terms of the conventional ones [18,19] as:

$$B_{20} = v - 2\sqrt{2}v' \quad (3)$$

* Corresponding author. Tel.: +86 13649273458.
E-mail address: weiaqun@163.com (Q. Wei).

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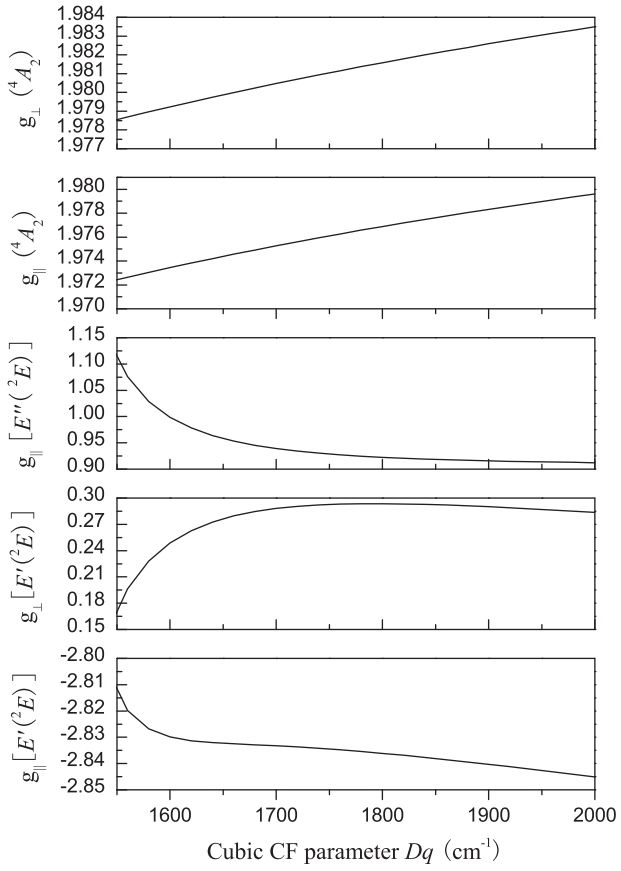

Fig. 1. The relationship between the g factors and the cubic CF parameter *Dq*.

$$B_{40} = -14Dq + \frac{4}{3}v + 2\sqrt{2}v' \tag{4}$$

$$B_{43} = -\sqrt{\frac{7}{10}}(20Dq + \frac{2}{3}v + \sqrt{2}v') \tag{5}$$

where Dq is the cubic CF parameter, whereas v and v' are the trigonal CF parameters [18]. The magnetic interactions can be given as [12]:

$$H_M = H_{SO}(\zeta) + H_{SOO}(M_0, M_2) + H_{SS}(M_0, M_2) + H_{OO}(M_0, M_2) \tag{6}$$

where ζ is the spin–orbit interaction parameter, whereas M_0 and M_2 are the Marvin's radial integrals [20] used for representing the SS, SOO and OO interactions. Our calculations for Hamiltonian matrix elements are carried out in the intermediate CF coupling scheme [21,22]. The method of calculations of the matrix elements of H_{ee}, H_{SO}, and H_{CF} has been described in [23], whereas those for H_{SS}, H_{SOO} and H_{OO} in [12,17].

Using the microscopic spin Hamiltonian theory, the ZFS parameter D and the g factors of the ground $^4A_2$ state of $3d^3$ ion in trigonal symmetry can be derived as:

$$D = \frac{1}{2}\{\varepsilon[E''(^4A_2)] - \varepsilon[E'(^4A_2)]\} \tag{7}$$

$$g_{\parallel}(^4A_2) = 2\langle\psi_{1/2}|kL_z + g_sS_z|\psi_{1/2}\rangle \tag{8}$$

$$g_{\perp}(^4A_2) = \langle\psi_{1/2}|kL_x + g_sS_x|\psi_{-1/2}\rangle, \tag{9}$$

where the symbols are defined as in [13,24].

The first excited ^2E state can be split by magnetic interactions into two two-fold-degenerate states $E'(^2E)$ and $E''(^2E)$. The zero field splitting of ^2E state is defined as:

$$\Delta(^2E) = \varepsilon[E'(^2E)] - \varepsilon[E''(^2E)] \tag{10}$$

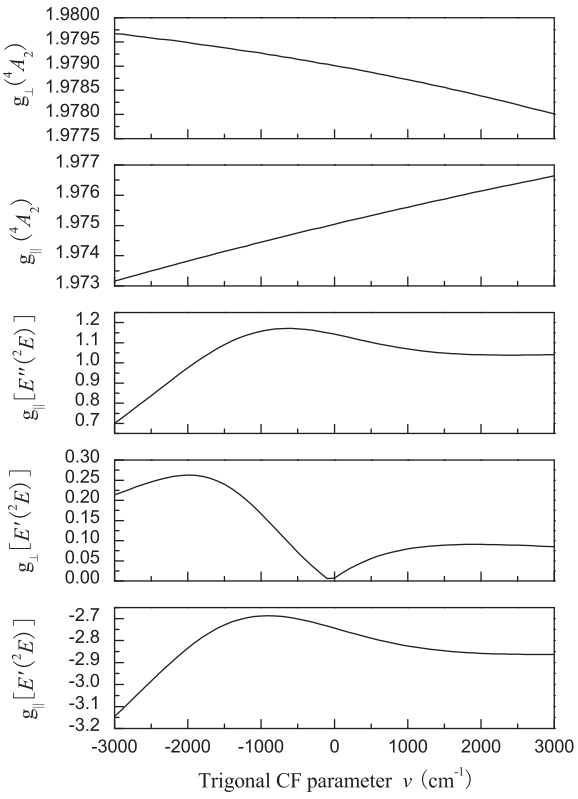

Fig. 2. The relationship between the g factors and the trigonal CF parameter v.

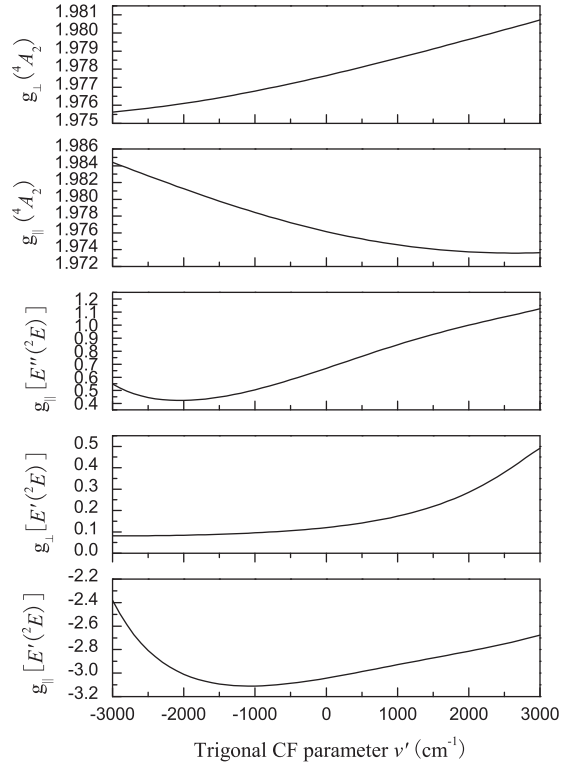

Fig. 3. The relationship between the g factors and the trigonal CF parameter v'.

For $E'(^2E)$ state, the g factors are defined by [10,25]:

$$g_{\parallel}[E'(^2E)] = 2\{k\langle E'_+|L_z|E'_+\rangle + g_s\langle E'_+|S_z|E'_+\rangle\}, \tag{11}$$

$$g_{\perp}[E'(^2E)] = 2\{k\langle E'_+|L_x|E'_-\rangle + g_s\langle E'_+|S_x|E'_-\rangle\}, \tag{12}$$