Theoretical studies of the Electron Paramagnetic Resonance parameters and local structure for the trigonal Yb^{3+} center in YAl$_3$(BO$_3$)$_4$ crystal

Hui-Ning Dong and Rong Zhang
College of Physics and Engineering,
Chengdu Normal University, Chengdu 611130, PR China,
e-mail: zhangrongcdnu@163.com

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Yttrium aluminium borate crystals have excellent physical and chemical properties. In this paper, the electron paramagnetic resonance g factors $g_{\|}$, $g_{\perp}$ of Yb^{3+} and hyperfine structure constants $A_{\|}$, $A_{\perp}$ of ^{171}Yb^{3+} and ^{173}Yb^{3+} isotopes in YAl$_3$(BO$_3$)$_4$ crystal are calculated from the perturbation formulas. The crystal field parameters are obtained from the superposition model and the crystal structure data. The electron paramagnetic resonance parameters for trigonal Yb^{3+} centers in YAl$_3$(BO$_3$)$_4$ are reasonably explained by considering the defect structures of doped Yb^{3+} centers. In the calculation, we also find that Yb^{3+} ion does not exactly reside in Y^{3+} site, but suffers an angle distortion $\Delta\theta(\approx 3.98^{\circ})$ with C$_3$ axis. The results are discussed.

Keywords: Electron Paramagnetic Resonance; crystal-field theory; superposition model analysis; Yb^{3+}; YAl$_3$(BO$_3$)$_4$

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1. Introduction

Yttrium aluminium borate YAl$_3$(BO$_3$)$_4$ crystals(YAB) have excellent physical and chemical properties such as high laser damage threshold, good chemical stability, broad transparency range, large nonlinear optical coefficients, proper refractive index dispersion for phase matching, high thermal and mechanical resistance, and so on [1-3]. It is interesting that YAB can be expediently doped with transition or rare earth impurity ions. In general, these above properties are closely related to the local structure and electronic states of the impurity ion in the host, which can be effectively investigated by means of electron paramagnetic resonance (EPR) technique. So many related experimental and theoretical works have been done in the past years [4-8]. For instance, EPR studies were carried out for Yb^{3+} doped YAl$_3$(BO$_3$)$_4$, the g factors $g_{\|}$ and $g_{\perp}$ and hyperfine structure constants were also measured for the trigonal Yb^{3+} center recently [8]. Dammk *et al*. calculated the EPR parameters by the method of crystal field theory. In the calculation, they directly used crystal field (CF) parameter which is not connected with the local crystal structure [9]. There are some mistakes found in their paper, for example, the wrong representation of the irreducible tensor operators lead directly to various errors in their calculation values of EPR parameters [10]. Li *et al*. not only recalculated the EPR values using the same CF parameters, but also theoretically studied the EPR parameters by the means of the first-principles [10]. Above theoretical results are also poor agreement with the experimental data, see Table I. As well known, the superposition model is mostly used in analysis of experimentally determined crystal field parameters. When the crystal structure of a magnetic ion is available, the SH principle is very expediently employed to study the local physical properties of the magnetic ion with its surrounding ligands. So in this paper, the EPR parameters are explained by the aid of the SH model and the perturbation formulas of 4f^{13} ion in trigonal symmetry. From these formulas, the EPR parameters $g_{\|}$ $g_{\perp}$ $A_{\|}$ and $A_{\perp}$ for Yb^{3+} center in YAl$_3$(BO$_3$)$_4$ crystal are reasonably explained and the angle distortion of impurity Yb^{3+} center is suggested. The results are discussed.

2. Calculation

The crystal structure of YAl$_3$(BO$_3$)$_4$ belongs to the space group $R32$ with three molecules per unit cell [11]. In this structure, the coordination polyhedron of Y^{3+}, Al^{3+}, and B^{3+} is trigonal prism, octahedra and triangles surrounded by the oxygen ions. The Yb^{3+} ionic radius (0.858 Å) is close to that of Y^{3+} (0.893 Å), whereas it is much larger than that of Al^{3+} (0.51 Å) or B^{3+} (0.23 Å) [12-13]. When Yb^{3+} is doped into the lattice of YAl$_3$(BO$_3$)$_4$ crystal, it can substitute for the octahedral Y^{3+} site and conserve the local trigonal symmetry, because of their similar ionic size, and no charge compensation is required [12]. In the following, the local structures of the Yb^{3+} centers are to be theoretically studied from the perturbation formulas of the EPR parameters.

The free Yb^{3+} ion has a 4f^{13} electronic configuration with a ^{2}F$_{7/2}$ ground state and a ^{2}F$_{5/2}$ excited state [14]. When Yb^{3+} ion is located on the Y^{3+} site of YAl$_3$(BO$_3$)$_4$ crystal, the free ion ground ^{2}F$_{7/2}$ and excited ^{2}F$_{5/2}$ states of free-ion splits into three and four Kramers doublets under trigonal symmetry crystal field, respectively. Because of the J-mixing between $J = 7/2$ and $J = 5/2$ states via crystal-field interaction, the basis wave function of ground doublet $\Gamma\gamma$(or $\Gamma\gamma'$) may be gained by diagonalizing the 14×14 energy matrix for 4f^{13} ion in trigonal symmetry field. Thus, one obtains

$$\begin{aligned}|\Gamma\gamma(\gamma')\rangle &= \sum_{M_{J1}} C(^2F_{7/2};\Gamma\gamma(or\gamma')M_{J1})|^2F_{7/2}M_{J1}) \\ &\quad \times |^2F_{7/2}M_{J1}\rangle + \sum_{M_{J2}} C(^2F_{5/2};\Gamma\gamma(or\gamma')M_{J2}) \\ &\quad \times |^2F_{5/2}M_{J2}\rangle, \qquad (1)\end{aligned}$$

where the subscript γ or γ' denote the two components of Γ irreducible representation. M_{J1} and M_{J2} are half-integers in the ranges $-7/2$ to $7/2$ and $-5/2$ to $5/2$, respectively [15]. The coefficients $C(^2F_{7/2};\Gamma\gamma(\gamma')M_{J1})$ or $C(^2F_{5/2};\Gamma\gamma(\gamma')M_{J2})$ can be determined by diagonalizing the 14×14 energy matrix containing the $^2F_{7/2}$ and $^2F_{5/2}$ states.

The perturbation Hamiltonian for the rare earth ion in the crystal under an external magnetic field can be expressed as [14]

$$\hat{H}' = \hat{H}_{SO} + \hat{H}_{CF} + \hat{H}_Z + \hat{H}_{hf} \qquad (2)$$

where $\hat{H}_{SO}$ is the spin-orbit coupling interaction and $\hat{H}_{CF}$ is the crystal field Hamiltonian. $\hat{H}_{SO}$ can be written as:

$$\hat{H}_{SO} = \zeta(\hat{L}\cdot\hat{S}) \qquad (3)$$

where ζ is the spin-orbit coupling coefficient, here $\zeta \approx 2907$ cm^{-1} [15], $\hat{L}$ and $\hat{S}$ are the orbital and spin momentum operators, respectively.

The crystal-field interaction Hamiltonian $\hat{H}_{CF}$ for a 4f^{13} ion may be written in terms of the irreducible tensor operators under trigonal symmetry [14]:

$$\begin{aligned}\hat{H}_{CF} &= B_2^0C_2^0 + B_4^0C_4^0 + B_4^3(C_4^3 - C_4^{-3}) \\ &\quad + B_6^0C_6^0 + B_6^3(C_6^3 - C_6^{-3}) + B_6^6(C_6^6 - C_6^{-6}) \qquad (4)\end{aligned}$$

where B_k^q ($k = 2, 4$ and $6; |q| \leq k$) are the crystal-field parameters.

The Zeeman interaction $\hat{H}_Z$ can be expressed in terms of the Lande factor g_J and the angular momentum operator $\hat{J}$ as [14]

$$\hat{H}_Z = g_J\mu_B\hat{H}\cdot\hat{J} \qquad (5)$$

and the hyperfine interaction term can be denoted as $\hat{H}_{hf} = P\mathrm{N}_J\hat{N}$, where P is the dipolar hyperfine structure constant, *i.e.*, P(^{171}Yb) $= 388.4(7) \times 10^{-4}$ cm^{-1} and P(^{173}Yb) $= -106.5(2) \times 10^{-4}$ cm^{-1}, the free ion values [15], N$_J$ is the diagonal matrix element for $^{2S+1}$L$_J$ state [14,15].

To study the EPR spectra and the local structure for YAl$_3$(BO$_3$)$_4$:Yb^{3+}, the perturbation formulas of the SH parameters for a 4f^{13} ion under trigonal symmetry are adopted [16]:

$$\begin{aligned}g_\parallel &= 2g_J\langle\Gamma\gamma|\hat{J}_Z|\Gamma\gamma\rangle \\ &\quad + 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{CF}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_Z|\Gamma\gamma\rangle}{E(\Gamma_X) - E(\Gamma)}, \\ g_\perp &= g_J\langle\Gamma\gamma|\hat{J}_+|\Gamma\gamma'\rangle \qquad (6)\end{aligned}$$

$$\begin{aligned}A_\parallel &= 2PN_j\langle\Gamma\gamma|\hat{J}_Z|\Gamma\gamma\rangle \\ &\quad + 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{CF}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma\gamma\rangle}{E(\Gamma_X) - E(\Gamma)} \\ A_\perp &= PN_J\langle\Gamma\gamma|\hat{N}_+|\Gamma\gamma'\rangle \qquad (7)\end{aligned}$$

Here g_J are the Lande factors for various $^{2S+1}$L$_J$ configurations, which are gained from Refs. 14 and 15. The operator $\hat{J}_+(= \hat{J}_X + i\hat{J}_\gamma)$ (or $\hat{N}_+(= \hat{N}_X + i\hat{N}_\gamma)$) stands for the linear combination of the $X-$ and $Y-$ components for the total angular momentum operator $\hat{J}$ (or $\hat{N}$) [14,15].

Based on the semi-empirical superposition model [17,18], the crystal field parameters B_k^q in Eq. (4) can be written as

$$B_k^q = \sum_{j=1}^{6} \bar{A}_k(R_0)(R_0/R_j)^{t_k}K_k^q(\theta_j,\varphi_j) \qquad (8)$$

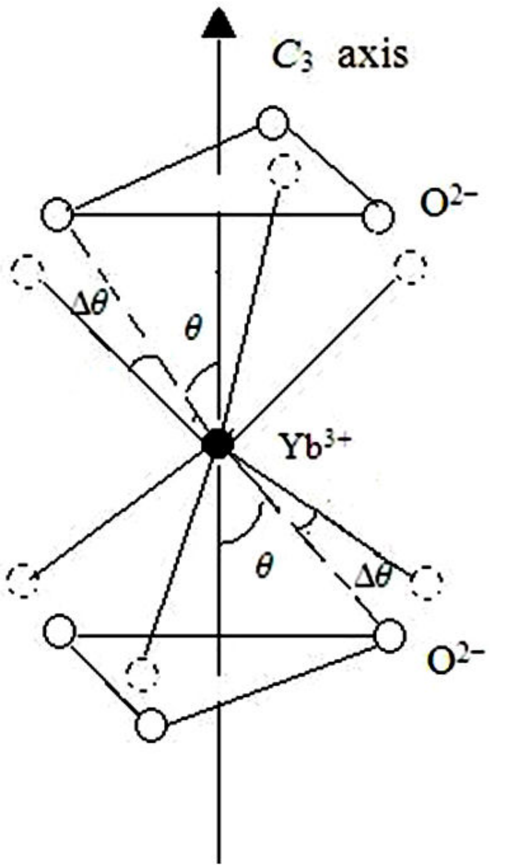

FIGURE 1. Local structure for the trigonal Yb^{3+} center in YAl$_3$(BO$_3$)$_4$. The impurity Yb^{3+} on the octahedral Y^{3+} site experiences the angle distortion $\Delta\theta(\approx 3.98^\circ)$.

Where the coordination factor $K_k^q(\theta_J, \phi_j)$ can be obtained from the local structural parameters of the studied system, t_k is the power law exponent, and $\bar{A}_k(R_0)$ is the intrinsic parameter with the reference distance R_0, which is usually taken as the average metal-ligand bond length. For [YbO$_6$]$^{9-}$ cluster, the superposition model parameters including t_k and $\bar{A}_k(R_0)$ are $t_2 = 3.5$, $t_4 = 6$, $t_6 = 6$, $\bar{A}_2(R_0) \approx -522$ cm^{-1}, $\bar{A}_4(R_0) \approx 66.3$ cm^{-1} and $\bar{A}_6(R_0) \approx 4.1$ cm^{-1} [16].

In the YAl$_3$(BO$_3$)$_4$ crystal, the host Y^{3+} ion is coordinated by six nearest-neighbour O^{2-} ions with the cation-anion distance $R_H \approx 2.302$ Å [14], the local structure data are given as follows: $\theta_1 = \theta_2 = \theta_3 \approx 55.188°$, $\varphi_1 \approx -157.911°$, $\varphi_2 \approx -37.911°$, $\varphi_3 \approx 82.089°$, $\theta_4 = \theta_5 = \theta_6 \approx 124.812°$, $\varphi_4 \approx -142.089°$, $\varphi_5 \approx -22.089°$, $\varphi_6 \approx -97.911°$, [12], see Fig. 1. When a impurity ion substitutes for a host ion, $R_j \neq R_H$ because of the different ionic radii of Yb^{3+} and the replaced Y^{3+} ion. The new cation-anion distance R$_j$ can be reasonably estimated from the approximate formula [19,20]

$$R_j = R_H + (r_i - r_h)/2 \tag{9}$$

where r_i and r_h are the ionic radii of impurity and the host ion, respectively. For YAl$_3$(BO$_3$)$_4$:Yb^{3+}, $r_i \approx 0.858$ Å, $r_h \approx 0.893$ Å [13]. Because of the covalency of Yb^{3+}-O^{2-} bonds, the orbital reduction factor k may be brought in, here $k \approx 0.866$.

When the host cation is replaced by the impurity in YAl$_3$(BO$_3$)$_4$ crystal, it can be expected that the local structure distortion $\Delta\theta$ would occur. Here it is taken as an adjustable parameter. When the above superposition model intrinsic parameters are substituted into Eqs.(6-7) and matching the calculated EPR parameters to experimental results, we have $\Delta\theta \approx 3.98°$. The comparisons between the calculated and experimental EPR parameters are shown in Table I.

3. Discussion

From Table I, one can find that by using the theoretical formulas of EPR parameters and the superposition model parameters given in this paper, the calculated results of EPR parameters $g_{\|}$, $g_{\perp}$, $A_{\|}$ and $A_{\perp}$ for Yb^{3+} ion at the trigonal Y^{3+} site in YAl$_3$(BO$_3$)$_4$ crystal based on the enhancive angle distortion $\Delta\theta$ show reasonable agreement with the observed data. Thus, these experimental data are reasonably explained, suggesting that the above formulas and these parameters adopted in this paper are reasonable.

Substitute the above superposition model intrinsic parameters into Eq. (8), the crystal field parameters are obtained and shown in Table II. These crystal field parameters are comparable to previous works. As mentioned before, the superposition model intrinsic parameters t_k and $\bar{A}_k(R_0)$ adopted in this paper are taken from the same impurity Yb^{3+} in Bi$_4$Ge$_3$O$_{12}$ crystal. Using these parameters and diagonalizing the complete 4f^{13} energy matrix in the trigonal field, the energy spectra are computed, which are the foundation of further calculation, see the Table III. One can find that the calculated energy levels reasonably coincide with the experimental results. So the data of the intrinsic parameters used in this paper can be regarded as acceptable.

TABLE I. EPR parameters for the trigonal Yb^{3+} center in YAl$_3$(BO$_3$)$_4$ crystal.

	$g_{\|}$	$g_{\perp}$	A$_{\|}$ (^{171}Yb)	A$_{\perp}$ (^{171}Yb)	A$_{\|}$ (^{173}Yb)	A$_{\perp}$ (^{173}Yb)
This work	3.6702	1.7014	959.4(30)	441.8(16)	263(2)	121(1)
Cal. [9]	3.257	2.042	838	529	231	-146
Cal. [10]	4.000	1.391	1032	360	285	99
Expt. [8]	3.612(1)	1.702(1)	958(1.6)	454(3.4)	–	–

TABLE II. The trigonal crystal-field parameters of Yb^{3+} in YAl$_3$(BO$_3$)$_4$. Crystal (in cm^{-1})

B_2^0	B_4^0	B_6^0	B_4^3	B_6^3	B_6^6	
767	-1002	263	-531	-147	71	Ref. [9]
338	-519	158	-274	-26	-90	Ref. [10]
681.8	-1026.7	129.6	643.4	-3.8	-53.0	This work

TABLE III. The crystal-field energy levels for Yb^{3+} in YAl$_3$(BO$_3$)$_4$ crystal (in cm^{-1})

	1	2	3	4	5	6	7
Cal	0	83	176	569	10194	10283	10666
Expt. [21]	0	94	185	581	10194	10277	10672

We find the local structure data of impurity Yb^{3+} including the cation-anion distance and the azimuthal angle of the oxygen atoms are different from those of the host Y^{3+} ion. The cation-anion distance of Yb^{3+}-O^{2-} can be reckoned by the aid of empirical equation Eq. (9). The azimuthal angle undergoes an angle distortion $\Delta\theta \approx 3.98^{\circ}$. This defect model of Yb^{3+} ion in $\mathrm{YAl_3(BO_3)_4}$ is similar to other rare or transition impurity ion in the same host crystal. Obviously, the theoretical result of the $\Delta\theta$ as well as the hyperfine structure constants of $^{173}\mathrm{Yb}^{3+}$ isotopes obtained in this work still remains to be further verified with experimental studies.

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