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# Analysis of the electron paramagnetic resonance zero-field splitting for $Fe^{3+}$ in sapphire

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The EPR zero-field splitting of $Fe^{3+}$ in a trigonal-symmetry crystal field has been calculated on the basis of the complete matrices for ligand-field spin-orbit coupling of the $d^5$ configuration with $C_3$ symmetry. The absorption spectrum, the EPR zero-field-splitting axial parameters $D$ and $F$, and the cubic parameter $a$ for the $Fe^{3+}$ ion in sapphire have been interpreted uniformly.

## I. INTRODUCTION

Since Van Vleck and Penney[1] first discussed the origin of the zero-field splitting of the $^6S$ state, many works have referred to it and great progress has been made.[2-6] Sharma discussed various mechanisms and he found that for $^6S$-state ions the most important contribution to the zero-field splitting is the associated effect of a low-symmetry crystal field and the spin-orbit-coupling interaction among the sextet, quartets, and doublets. In the present paper, we perform a theoretical calculation of the ground-state EPR zero-field-spitting parameters $D$, $F$, and $a$ for $Fe^{3+}$ in sapphire by employing the complete matrices for the ligand-field spin-orbit-coupling perturbation of the $d^5$ configurations with $C_3$ symmetry, which are $\Gamma_4$, $\Gamma_5$, and $\Gamma_6$ for the sextet, quartets, and doublets.

## II. THEORETICAL ANALYSIS

### A. EPR parameters $D$, $F$, and $a$

The EPR experimental spectrum of $Fe^{3+}$ in a trigonal crystal field can be analyzed in terms of the spin Hamiltonian given by Bleaney and Trenam,[7]

$$\begin{aligned}\hat{H}_s = {} & g\beta \mathbf{H}\cdot\mathbf{S}+D[S_z^2-S(S+1)/3]+a[S_\xi^4+S_\eta^4+S_\zeta^4-S(S+1)(3S^2+3S-1)/5]/6\\ & +F[35S_z^4-30S(S+1)S_z^2+25S_z^2-6S(S+1)+3S^2(2+1)^2]/180\ . \end{aligned} \tag{1}$$

Parameters $D$ and $F$ are associated with second- and fourth-order spin operators, respectively, and represent a component of the crystalline electric field which is axially symmetric about the $C_3$ axis; parameter $a$ is associated with a fourth-order spin operator and represents a cubic component of the crystalline electric field. From Eq. (1) the explicit expression for the $^6S$-state splitting energy can be written as

$$\begin{aligned} E(\pm\tfrac{1}{2}) &= D/3-(a-F)/2\\ &\quad -[(18D+a-F)^2+80a^2]^{1/2}/6\ ,\\ E(\pm\tfrac{3}{2}) &= -2D/3+(a-F)\ ,\\ E(\pm\tfrac{5}{2}) &= D/3-(a-F)/2\\ &\quad +[(18D+a-F)^2+80a^2]^{1/2}/6\ , \end{aligned} \tag{2}$$

where $E(\pm\frac{3}{2})$ corresponds to the energy of the $\Gamma_6$ state, and $E(\pm\frac{1}{2})$ and $E(\pm\frac{5}{2})$ to $\Gamma_4$ or $\Gamma_5$. The parameters $D$, $F$, and $a$ for $Fe^{3+}$ in sapphire can be determined by using Eq. (2) and taking a cubic approximation.

### B. Energy matrices

Crystal-field spin-orbit-coupling matrices for the $d^1$, $d^2$, $d^3$, $d^4$, and $d^5$ configurations have been discussed by many workers,[8-11] but there has been no work concerning the complete matrices for the $d^5$ configuration with $C_3$ symmetry. In this work Dunn's method and formulas are used to determine the matrix elements for the perturbation Hamiltonian

$$\hat{H}=\tfrac{1}{2}\sum_{i,j} e^2/r_{ij}+\zeta\sum_i l_i S_i+\sum_i V_i\ , \tag{3}$$

where $\zeta$ is the one-electron spin-orbit coupling coefficient and $V_i$ is the ligand potential

$$\begin{aligned} V_i = {} & v_{20}r_i^2 Z_{20}(\theta_i,\phi_i)+v_{40}r_i^4 Z_{40}(\theta_i,\phi_i)\\ & +v_{43}^c r_i^4 Z_{43}^c(\theta_i,\phi_i)+v_{43}^s r_i^4 Z_{43}^s(\theta_i,\phi_i)\ . \end{aligned} \tag{4}$$

The matrix elements are composed of the Racah parameters $B$, $C$, the spin-orbit coupling-coefficient $\zeta$, the Trees correction,[12] the Racah correction,[13] and the crystal-field parameters which are of the form

$$\begin{aligned} &Y_1=\tfrac{1}{7}(5/4\pi)^{1/2}v_{20}\langle r^2\rangle,\quad Y_2=\tfrac{1}{7}(1/4\pi)^{1/2}v_{40}\langle r^4\rangle\ ,\\ &Y_3=(5/28\pi)^{1/2}v_{43}^c\langle r^4\rangle,\quad Y_4=(5/28\pi)^{1/2}v_{43}^s\langle r^4\rangle\ . \end{aligned} \tag{5}$$

The parameters $v_{kq}^\xi$ are of the same form as those used by Shen and Zhao,[14] $Z_{kq}^\xi(\theta_i,\phi_i)$ and $Z_{kq}^\xi(\theta_i,\phi_i)$ denote real spherical harmonic functions, and $r_i$, $\theta_i$, $\phi_i$ are the coordinates of the $d$ electrons.

## III. $d$-$d$ TRANSITION SPECTRUM AND EPR ZERO-FIELD SPLITTING OF $Fe^{3+}$ IN SAPPHIRE

By using the average covalency parameter[6,15] $N$, we have

$$B=N^4B_0,\ C=N^4C_0,\ \zeta=N^2\zeta_0,\ \alpha=N^4\alpha_0,\ \beta=N^4\beta_0\ , \tag{6}$$

TABLE I. Comparison between calculated and experimental values for the zero-field splitting (ZFS) of the $^6S$ state of sapphire $Al_2O_3$:$Fe^{3+}$. All are in units of $10^{-4}$ cm$^{-1}$.

| ZFS | Calc. | Expt. |
|---|---|---|
| $E(\pm\frac{5}{2})-E(\pm\frac{1}{2})$ | 10307 | 10451[a] |
| $E(\pm\frac{3}{2})-E(\pm\frac{1}{2})$ | 3974 | 4014 |
| $D$ | 1694 | 1719 |
| $a$ | 259 | 236 |
| $a-F$ | 343 | 339 |

[a] Lee, Brodbeeck, and Yang (Ref. 17).

where the Racah parameters $B_0=1050$ cm$^{-1}$, $C_0=3806$ cm$^{-1}$, the spin-orbit coupling coefficient $\zeta_0=440$ cm$^{-1}$, the Trees correction $\alpha_0=170$ cm$^{-1}$, and the Racah correction $\beta_0=-131$ cm$^{-1}$ are determined by the spectrum of the free $Fe^{3+}$ ion.[16] We have obtained the EPR zero-field-splitting axial parameters $D$ and $(a-F)$, the cubic parameter $a$, and the $d$-$d$ transition spectrum for $Fe^{3+}$ in sapphire by diagonalizing the complete matrices. The comparison between the theory and the experimental findings are given in Tables I and II, respectively.

### IV. RESULT AND DISCUSSION

As remarked by Bleaney and Trenam,[7] at 0° and 90° the magnetic field $H$ is along a cubic axis of the crystal, where the effect of the first-order term in $D$ in the splitting is zero, while that of the cubic-field term in $a$ is large, assuming the axes of the cubic field nearly coincide with those of the crystal. We determine the cubic parameter $a$ by employing a cubic approximation, in which $R_j$ is equal to a constant and angle $\theta_j$ is equal to 54.74°. In this case, the theoretical values for $D$ and $F$ are equal to zero, respectively, so that the approximation is a reasonable one, corresponding to the experimental method.

TABLE III. The influence of parameter $a$ on $D$ and $a-F$. All are units of $10^{-4}$ cm$^{-1}$.

| $a$ | $D$ | $a-F$ |
|---|---|---|
| 500 | 1681 | 334 |
| 450 | 1684 | 337 |
| 400 | 1687 | 339 |
| 350 | 1690 | 340 |
| 300 | 1692 | 342 |
| 250 | 1694 | 343 |
| 200 | 1695 | 344 |
| 150 | 1697 | 345 |
| 100 | 1697 | 346 |
| 50 | 1698 | 346 |
| 0 | 1698 | 346 |

The EPR zero-field-splitting axial parameters $D$ and $F$ are due to the associated effect of the low-symmetry crystal field and the spin-orbit-coupling interaction among the sextet, quartets, and doublets; they are very sensitive to distortion of the octahedron,[20] and can be determined by the splitting energy. From Table III we see that the splitting parameters $D$ and $(a-F)$ are insensitive to a change of the parameter $a$; therefore, in the general case, the parameters $D$ and $(a-F)$ can be calculated by the following formulas:

$$\begin{aligned} 6D+(a-F)/3&=E(\pm\tfrac{5}{2})-E(\pm\tfrac{1}{2})\ , \\ 2D+5(a-F)/3&=E(\pm\tfrac{3}{2})-E(\pm\tfrac{1}{2})\ . \end{aligned} \tag{7}$$

The absorption spectrum of $Fe^{3+}$ given in Table II is only for the center of gravity as represented by Low and Rosengarten,[21] and the spin-orbit coefficient used here is equal to 367.6 cm$^{-1}$ as defined by the relationship[6] $\zeta=N^2\zeta_0$, which is less than the experimental finding (440 cm$^{-1}$), and is also less than that used by Low and Rosen-

TABLE II. Comparison between calculated and experimental values for the $d$-$d$ transition of sapphire $Al_2O_3$:$Fe^{3+}$. All levels in units of cm$^{-1}$.

| | Calc. (trigonal) | | Calc. (cubic) | Expt. | |
|---|---|---|---|---|---|
| $^6S$-$^4A_2T_1(G)$ | 9224[a] | $^4T_1(G)$ | 9697[b] | 9450[c] | 9450[d] |
| $^4ET_1(G)$ | 9834 | | | | |
| $^4A_1T_2(G)$ | 14380 | $^4T_2(G)$ | 14876 | 14350 | 14350 |
| $^4ET_2(G)$ | 15238 | | | | |
| $^4EE(G)$ | 22885 | $^4A_1(G)$ | 22981 | 22270 | 22120 |
| $^4A_1A_1(G)$ | 22981 | $^4E(G)$ | | | |
| $^4ET_2(D)$ | 24532 | $^4T_2(D)$ | 24632 | 25510 | 25680 |
| $^4A_1T_2(D)$ | 24647 | | | | |
| $^4EE(D)$ | 26350 | $^4E(D)$ | 26449 | 26800 | 26570 |
| $^4A_2T_1(P)$ | 32067 | $^4T_1(P)$ | 32100 | 29800 | 29000 |
| $^4ET_1(P)$ | 32354 | | | | |

[a] Nonvanishing crystal parameters $Y_1=282.7117$, $Y_2=-874.1319$, $Y_3=6968.309$ cm$^{-1}$.
[b] Nonvanishing crystal parameters $Y_2=-957.2024$, $Y_3=6768.444$ cm$^{-1}$.
[c] Krebs and Maisch (Ref. 18).
[d] Lehmann and Harder (Ref. 19).

garten[21] (420 $\mathrm{cm}^{-1}$); therefore, our result contradicts the expectation of Low and Rosengarten that it is possible to fit the optical spectrum and the initial ground-state splitting by assuming a spin-orbit coupling which is 20%–30% larger than the free-ion spin-orbit-coupling coefficient.

To conclude, a general procedure for calculating the EPR zero-field-splitting parameters $D$, $a$, and $(a-F)$ simultaneously is proposed on the basis of the complete matrices for ligand-field spin-orbit-coupling perturbation obtained by us, and the EPR spectrum and the absorption spectrum for $\mathrm{Fe}^{3+}$ in sapphire have been interpreted uniformly.

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