

Optical absorption and EPR study of the octahedral Fe³⁺ center in yttrium aluminum garnet

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The optical-absorption and EPR spectra of octahedral Fe³⁺ center in yttrium aluminum garnet have been studied by diagonalizing the complete energy matrices for a d^5 configuration ion in a trigonal ligand field. It is shown that the local lattice structure around an octahedrally coordinated Fe³⁺ center has an expansion distortion. The expansion distortion may be attributed to the fact that the radius of Fe³⁺ ion is larger than that of Al³⁺ ion, and the Fe³⁺ ion will push the oxygen ligands outwards. Simultaneously, the local lattice structure distortion parameters $\Delta R=0.0907$ Å and $\Delta\theta=1.940^\circ$ for the octahedral Fe³⁺ center in the crystal are determined. From optical spectra calculation, we confirm that two strong sharp transitions at 407 and 415 nm, which are apparent in the optical absorption spectra for lightly doped YAG:Fe³⁺ system, should be ascribed to the tetrahedral Fe³⁺ center. This is also in accord with the conclusion of Rotman *et al.* [J. Appl. Phys. **66**, 3207 (1989)].

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I. INTRODUCTION

Yttrium aluminum garnet (YAG) doped with transition-metal ions (Nd³⁺, Fe³⁺, Cr⁴⁺, etc.) is the most important crystal material for solid-state lasers that are widely used in medical, commercial, military, and industrial applications.¹⁻⁴ However, only the Fe³⁺ impurity in the crystal contribute to the optical absorption near the band edge and influence the UV optical properties of the material. In order to understand the influence of this impurity on the material's properties, the YAG:Fe³⁺ system has been extensively studied during the past several decades.⁵⁻¹³ For example, the EPR spectra of Fe³⁺ impurity in YAG, which is very sensitive to distortion of the local lattice structure around the paramagnetic ion, had been measured by Rimai and Kushida.⁵ The results indicate that the Fe³⁺ ion substitutes for the Al³⁺ ion at both octahedral and tetrahedral sites which have C_{3i} and S_4 symmetry, respectively. The optical absorption spectra of Fe³⁺ impurities in the crystal have also been examined.^{6,7} It is found that two sharp absorption peaks at 407 and 415 nm are obvious in the optical absorption spectra. Rotman *et al.*¹⁰ proved that both peaks are associated with the excitation of the electron in 6A_1 ground state of Fe³⁺ ion to higher states, and these authors believe that both peaks arise from the tetrahedral sites. Nevertheless, Sugitani *et al.*⁶ analyzed the absorption spectra and concluded that the shorter-wavelength peak was due to Fe³⁺ at an octahedral site, while the longer-wavelength peak was due to Fe³⁺ at a tetrahedral site. In general, the local lattice structure around the impurity ion is assumed to be the same as that of the undistorted host crystal. By using this assumption, Yu¹² has shown that the calculated value of the EPR parameter, D , of tetrahedral Fe³⁺ center in YAG is two times larger than the experimental value. For the EPR parameter D of the octahedral Fe³⁺ center, Febbraro⁹ got a reproduction of the experimental data. However, it is well known that for a d^5 configuration ion in a

trigonal ligand field, the high-spin ground state is the 6A_1 state. To describe the 6A_1 ground-state splitting, the spin Hamiltonian should include three different EPR parameters a , D , and $(a-F)$. The parameter a relates to a fourth-order spin operator and represents a cubic component of the crystalline electric field. The parameters D and $(a-F)$ are, respectively, associated with the second-order and fourth-order spin operators and represent an axial component of the crystalline electric field. When we substitute Febbraro's optical parameters⁹ (B , C , Dq , and ζ) for the octahedral Fe³⁺ center into our complete matrices, our calculation shows that the theoretical EPR cubic parameter a will deviate far from the experimental finding. So far, a unified explanation has not been presented for the optical absorption and EPR spectra of Fe³⁺ in YAG. Since the radius of Fe³⁺ ion is obviously larger than that of Al³⁺ ion, the local lattice structure of the Fe³⁺ in YAG:Fe³⁺ should be different from that of the Al³⁺ in YAG. In the present paper, by considering the distortion of the local lattice structure, the optical absorption and EPR spectra of octahedral Fe³⁺ center in YAG will be studied simultaneously on the basis of the complete energy matrices for a d^5 configuration ion in a trigonal ligand field. Furthermore, the study of optical spectra is based on the actual symmetry instead of a cubic approximation. This is different from any previous study of the optical spectra.

II. THEORY

It is well known that the EPR spectra of d^5 configuration Fe³⁺ ion in a trigonal ligand field can be analyzed by employing the spin Hamiltonian,¹⁴

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

where a is the cubic-field splitting parameter; D and $(a-F)$ correspond to the low-symmetry second-order and fourth-order components, respectively. From Eq. (1) the energy levels in 6A_1 state for a zero magnetic field can be written as

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

Then, the zero-field splitting energies, ΔE_1 and ΔE_2 , in the ground 6A_1 state may be expressed as a function of the EPR parameters a , D , and $(a-F)$ (Ref. 15),

$$\begin{aligned} \Delta E_1 &= (\pm 1/3)[(18D + a - F)^2 + 80a^2]^{1/2}, \\ \Delta E_2 &= (3/2)(a - F) - D \pm (1/6)[(18D + a - F)^2 + 80a^2]^{1/2}, \end{aligned} \quad (3)$$

where the positive and negative signs correspond to $D \geq 0$ and $D < 0$, respectively.

The perturbation Hamiltonian for a d^5 configuration ion in a trigonal ligand field can be written as¹⁶

$$\hat{H} = \hat{H}_{ee} + \hat{H}_{so} + \hat{H}_{lf} = \sum_{i < j} e^2/r_{ij} + \zeta \sum_i l_i \cdot s_i + \sum_i V_i, \quad (4)$$

where the first term is the electron-electron interactions; the second term is the spin-orbit coupling interactions; the third term is the ligand-field potentials that may be expressed as

$$\begin{aligned} V_i &= \gamma_{00}Z_{00} + \gamma_{20}r_i^2Z_{20}(\theta_i, \phi_i) + \gamma_{40}r_i^4Z_{40}(\theta_i, \phi_i) \\ &\quad + \gamma_{43}^c r_i^4 Z_{43}^c(\theta_i, \phi_i) + \gamma_{43}^s r_i^4 Z_{43}^s(\theta_i, \phi_i), \end{aligned} \quad (5)$$

where r_i , θ_i , and ϕ_i are spherical coordinates of the i th electron. Z_{lm} , Z_{lm}^c , and Z_{lm}^s are defined as

$$\begin{aligned} Z_{l0} &= Y_{l0}, \\ Z_{lm}^c &= (1/\sqrt{2})[Y_{l,-m} + (-1)^m Y_{l,m}], \\ Z_{lm}^s &= (i/\sqrt{2})[Y_{l,-m} - (-1)^m Y_{l,m}]. \end{aligned} \quad (6)$$

The Y_{lm} in Eq. (6) are the spherical harmonics. γ_{l0} , γ_{lm}^c , and γ_{lm}^s are associated with the local lattice structure around d^5 -configuration ion by the relations

$$\begin{aligned} \gamma_{l0} &= -\frac{4\pi}{2l+1} \sum_{\tau=1}^n \frac{eq_{\tau}}{R_{\tau}^{l+1}} Z_{l0}(\theta_{\tau}, \varphi_{\tau}), \\ \gamma_{lm}^c &= -\frac{4\pi}{2l+1} \sum_{\tau=1}^n \frac{eq_{\tau}}{R_{\tau}^{l+1}} Z_{lm}^c(\theta_{\tau}, \varphi_{\tau}), \end{aligned}$$

$$\gamma_{lm}^s = -\frac{4\pi}{2l+1} \sum_{\tau=1}^n \frac{eq_{\tau}}{R_{\tau}^{l+1}} Z_{lm}^s(\theta_{\tau}, \varphi_{\tau}), \quad (7)$$

where θ_{τ} and φ_{τ} are angular coordinates of the ligand. τ and q_{τ} represent the τ th ligand ion and its effective charge, respectively. R_{τ} denotes the impurity-ligand distance.

On the basis of the irreducible representations $\Gamma_4(\Gamma_5)$ and Γ_6 of the C_3^* double group, two 84×84 energy matrices for a d^5 -configuration ion corresponding to the perturbation Hamiltonian (4) have been derived.¹⁶ The matrix elements are the function of the Racah parameters B and C , the spin-orbit coupling coefficient ζ , and the ligand-field parameters that have the following forms:¹⁷

$$\begin{aligned} B_{20} &= (5/4\pi)^{1/2} \gamma_{20} \langle r^2 \rangle, \\ B_{40} &= (9/4\pi)^{1/2} \gamma_{40} \langle r^4 \rangle, \\ B_{43}^c &= (9/8\pi)^{1/2} \gamma_{43}^c \langle r^4 \rangle, \\ B_{43}^s &= i(9/8\pi)^{1/2} \gamma_{43}^s \langle r^4 \rangle. \end{aligned} \quad (8)$$

For octahedral Fe^{3+} centers in $\text{YAG}:\text{Fe}^{3+}$ system, the local symmetry is C_{3i} point group. According to the superposition model, the ligand-field parameter B_{43}^s will disappear and the other terms can be derived as

$$\begin{aligned} B_{20} &= 3G_2(\tau)(3 \cos^2 \theta - 1), \\ B_{40} &= (3/4)G_4(\tau)(35 \cos^4 \theta - 30 \cos^2 \theta + 3), \\ B_{43}^c &= (3\sqrt{35}/2)G_4(\tau) \sin^3 \theta \cos \theta, \end{aligned} \quad (9)$$

where

$$\begin{aligned} G_2(\tau) &= -eq_{\tau} G^2(\tau), \\ G_4(\tau) &= -eq_{\tau} G^4(\tau), \end{aligned}$$

$$G^k(\tau) = \int_0^R R_{3d}^2(r) r^2 \frac{r^k}{R^{k+1}} dr + \int_R^{\infty} R_{3d}^2(r) r^2 \frac{R^k}{r^{k+1}} dr. \quad (10)$$

The R in Eq. (10) and θ in Eq. (9) denote the Fe-O distance and the angle between Fe-O bond and C_3 axis, respectively. According to the Van Vleck approximation for $G^k(\tau)$ integral and using the point charge model,¹⁸ we obtain the following relations:

$$\begin{aligned} G_2(\tau) &= -\frac{eq_{\tau} \langle r^2 \rangle}{R^3}, \\ G_4(\tau) &= -\frac{eq_{\tau} \langle r^4 \rangle}{R^5}. \end{aligned} \quad (11)$$

With the use of Eqs. (9) and (11), the relationship between the local lattice structure of octahedral Fe^{3+} center in $\text{YAG}:\text{Fe}^{3+}$ system and its optical spectrum as well as the EPR parameters can be studied by employing the complete energy matrices.

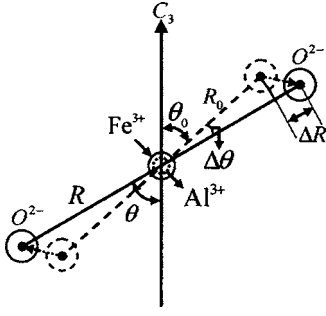


FIG. 1. Local structure distortion of octahedral Fe^{3+} center in $\text{YAG}:\text{Fe}^{3+}$ system.

III. CALCULATIONS

The structure of YAG is very similar to that of yttrium iron garnet. When Fe^{3+} impurities are doped in YAG, a number of Fe^{3+} impurities will replace the Al^{3+} ions in the octahedral site. The local lattice structure around the octahedral Fe^{3+} center displays a trigonal distortion.⁵ The trigonal distortion can be described by employing two parameters ΔR and $\Delta\theta$ as shown in Fig. 1. If one uses R_0 and θ_0 to represent the Al-O bond length and the angle between Al-O bond and C_3 axes of the host crystal YAG, respectively, then the local structure parameters R and θ for the octahedral Fe^{3+} center in $\text{YAG}:\text{Fe}^{3+}$ system may be expressed as

$$\begin{aligned} R &= R_0 + \Delta R, \\ \theta &= \theta_0 + \Delta\theta \end{aligned} \quad (12)$$

with $R_0=1.937 \text{ \AA}$ and $\theta_0=50.284^\circ$.¹⁹ According to the point-charge model, the effective charge of the oxygen ligand was studied and its value is from $-0.98e$ to $-1.14e$.²⁰ Moreover, Van Vleck found that the effective charge of the oxygen ligand is $-1.01e$.²¹ Here, Van Vleck's value, $q_r=-1.01e$, is taken in our calculation. By using the radial wave function of Fe^{3+} in complexes,²² the values of $\langle r^2 \rangle$ and $\langle r^4 \rangle$ can be estimated as follows:

$$\begin{aligned} \langle r^2 \rangle &= 2.6572 \text{ a.u.}, \\ \langle r^4 \rangle &= 27.3895 \text{ a.u.} \end{aligned} \quad (13)$$

In this case, the trigonal ligand-field parameters (B_{20}, B_{40}, B_{43}^c) are only functions of ΔR and $\Delta\theta$. In order to decrease the number of adjustable parameters and to reflect the effects of covalency, we take an average covalence factor N (Ref. 23) and use the following relationship:

$$B = N^4 B_0, \quad C = N^4 C_0, \quad \zeta = N^2 \zeta_0, \quad (14)$$

where $B_0=1050 \text{ cm}^{-1}$, $C_0=3806 \text{ cm}^{-1}$, and $\zeta_0=440 \text{ cm}^{-1}$ are the free- Fe^{3+} ion parameters.^{24,25} For the $\text{YAG}:\text{Fe}^{3+}$ system, by diagonalizing the complete energy matrices, the optical spectra and ground state zero-field splitting, which can be calculated from the EPR parameters and Eq. (3), may be simulated with use of distortion parameters ΔR , $\Delta\theta$, and the covalence factor N . We finally obtained both the optical spectra and the EPR ground-state zero-field splitting by adjusting the parameters ΔR , $\Delta\theta$, and N . Simultaneously, the

TABLE I. The observed and calculated optical spectra for Fe^{3+} in $\text{YAG}:\text{Fe}^{3+}$ system.

Observed ^a (cm^{-1})	Calculated (oct) ^b (cm^{-1})	Transition
10400	10312	${}^4E^4T_{1g}(G)$
14300	14347	${}^4A_1{}^4T_{2g}(G)$
16000		
19400		
20460	20462	${}^4E^4E_g(G)$
20510	20505	${}^4A_1{}^4A_{1g}(G)$
21180		
22880	22951	${}^4E^4T_{2g}(D)$
24030 ^c		
24440 ^c		
25200		
25540	25506	${}^4E^4E_g(D)$
25870		
26300		
26670		

^aSpectra data obtained from Ref. 7.

^b $B=729 \text{ cm}^{-1}$, $C=2643 \text{ cm}^{-1}$, $\Delta R=0.0907 \text{ \AA}$, and $\Delta\theta=1.940^\circ$.

^cTwo sharp absorption peaks.

distortion parameters $\Delta R=0.0907 \text{ \AA}$, $\Delta\theta=1.940^\circ$ and covalence factor $N=0.9129$ (i.e., $B=729 \text{ cm}^{-1}$, $C=2643 \text{ cm}^{-1}$, and slightly adjusted $\zeta=370.8 \text{ cm}^{-1}$) are determined. All results are listed in Tables I and II.

It can be seen from Tables I and II that the theoretical values are in good agreement with experimental values. The distortion parameters $\Delta R=0.0907 \text{ \AA}$ and $\Delta\theta=1.940^\circ$ may provide a unified explanation for the experimental findings of optical absorption spectra and EPR. This $\Delta R > 0$ means that the local lattice structure around the octahedral Fe^{3+} center in $\text{YAG}:\text{Fe}^{3+}$ system has an expansion distortion. The expansion distortion may be attributed to the fact that the radius of Fe^{3+} ion ($r=0.64 \text{ \AA}$) is bigger than that of Al^{3+} ion ($r=0.50 \text{ \AA}$),²⁶ and the Fe^{3+} ion will push the oxygen ligands outwards. On the other hand, it is well known that the optical absorption spectra originate from octahedral and tetrahedral Fe^{3+} centers in $\text{YAG}:\text{Fe}^{3+}$ system. In lightly doped $\text{YAG}:\text{Fe}^{3+}$ system, two sharp absorption peaks¹⁰ at 407 and 415 nm (i.e., $24\,096$ and $24\,570 \text{ cm}^{-1}$) were apparent in the optical absorption spectra. However, our calculation for octahedral Fe^{3+} centers shows that the doublet does not occur in the calculated results as shown in Table I. From the calculated results, we may confirm that the characteristic doublet should be ascribed to the tetrahedral Fe^{3+} center in $\text{YAG}:\text{Fe}^{3+}$ system. Our results support the conclusion of Rotman *et al.*¹⁰

IV. CONCLUSION

The EPR and optical-absorption spectra of octahedral Fe^{3+} center in $\text{YAG}:\text{Fe}^{3+}$ system have been studied by means of the complete energy matrices for a d^5 configuration

TABLE II. The ground-state zero-field splitting ΔE_1 , ΔE_2 and the EPR parameters a , D , and $(a-F)$ for the octahedral Fe^{3+} center in YAG as a function of ΔR and $\Delta\theta$.^a

ΔR (Å)	$\Delta\theta$ (deg)	$10^4\Delta E_1$ (cm^{-1})	$10^4\Delta E_2$ (cm^{-1})	10^4a (cm^{-1})	10^4D (cm^{-1})	10^4F (cm^{-1})	$10^4(a-F)$ (cm^{-1})
0.0800	2.004	-6523.0	-1860.4	205	-1093.8	0.1	204.9
0.0800	2.044	-6416.2	-1824.8	205	-1075.9	0.1	204.9
0.0800	2.093	-6288.0	-1782.7	205	-1054.4	0.4	204.6
0.0800	2.133	-6181.8	-1747.6	205	-1036.6	0.5	204.5
0.0907	1.900	-6388.4	-1858.2	205	-1069.7	27.9	177.1
0.0907	1.940	-6288.8	-1825.8	205	-1053.0	27.9	177.1
0.0907	1.980	-6190.0	-1793.1	205	-1036.5	28.0	177.0
0.1000	1.765	-6382.6	-1886.8	205	-1067.7	47.1	157.9
0.1000	1.805	-6287.3	-1855.6	205	-1051.7	47.4	157.6
0.1000	1.846	-6190.1	-1823.1	205	-1035.4	47.3	157.7
0.1000	1.886	-6095.8	-1792.3	205	-1019.6	47.7	157.3
Expt. (Ref. 5)		-6288.4	-1824.2	205	-1053	27	178

^a $B=729 \text{ cm}^{-1}$, $C=2643 \text{ cm}^{-1}$, $\Delta R=0.0907 \text{ Å}$, $\Delta\theta=1.940^\circ$, and $\zeta=370.8 \text{ cm}^{-1}$.

ion in a trigonal ligand field. It is shown that the local lattice structure around octahedral Fe^{3+} center has an expansion distortion. The expansion distortion may be ascribed to the fact that the radius of Fe^{3+} ion is larger than that of Al^{3+} ion, and the Fe^{3+} ion will push the oxygen ligands outwards. Furthermore, the local structure parameters $R=2.0277 \text{ Å}$ and $\theta=52.224^\circ$ for octahedral Fe^{3+} center in the crystal are determined. From our calculation, we confirm that two strong sharp transitions at 407 and 415 nm originate from the tetra-

hedral Fe^{3+} center. This result is also in agreement with the conclusion of Rotman *et al.*¹⁰

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