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EPR parameters and defect structures for two trigonal Er^{3+} centers in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals

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In this paper, the perturbation formulas of EPR parameters (g factors $g_\parallel, g_\perp$ and hyperfine structural constants $A_\parallel$ and $A_\perp$) for the lowest Kramers doublet Γ_6 or Γ_7 of $^4I_{15/2}$ of $4f^{11}$ ion in trigonal symmetry are established. In these formulas, the second-order perturbation contributions are considered in addition to the first-order perturbation contributions considered in the previous works. Based on these formulas, the EPR parameters and the defect structures of two trigonal Er^{3+} centers in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals are studied. It is found that in order to reach a good fit between calculations and experiments, the Er^{3+} ions in centers I and II do not occupy exactly the Li^+ and Nb^{5+} sites, respectively, but are displaced along the C_3 axis away from the center of oxygen octahedron by about 0.039 nm for center I and towards the center of octahedron by about 0.030 nm for center II. The reasonableness of the local lattice distortions and the contributions from the second-order perturbation terms are discussed.

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I. INTRODUCTION

$LiNbO_3$ single crystals have been an attractive materials due to the combination of excellent electro-optical, acousto-optical, piezoelectric, elasto-optic, photorefractive effects, and the applications in integrated optics to create various components, such as modulators, wavelength filters, and low-loss optical waveguides.[1–3] Recently, Er^{3+}-doped $LiNbO_3$ has gained attention through the development of light amplifiers based on $LiNbO_3{:}Er^{3+}$.[4–7] Since the knowledge of occupation position and defect structure of impurity ion is very helpful to understand the physical properties of the doped materials and electron paramagnetic resonance (EPR) is a suitable method to study the occupation position and defect structure of impurity ion, many EPR experimental works have been done on Er^{3+} impurity in $LiNbO_3$ crystals, e.g., Dierolf *et al.*[8] and Milori *et al.*[9] found one trigonal Er^{3+} center (marked as center I) in $LiNbO_3$, with considerable anisotropy of g factors which was attributed to Er^{3+} occupying the Li^+ position. For MgO or ZnO codoped $LiNbO_3{:}Er^{3+}$ crystals Bravo *et al.*[10] found a new trigonal Er^{3+} center (marked as center II) with relatively smaller anisotropy of g factors in addition to the previous observed center I. Center II was regarded as Er^{3+} occupying Nb^{5+} position in these codoped $LiNbO_3$ crystals.[10]

Up to now, however, the above experimental results have not been satisfactorily explained, and the defect structure of these Er^{3+} centers (particularly, center II) have not been obtained by analyzing the EPR data either. For example, Milori *et al.*[9] roughly studied the g factors of center I by considering only the interactions within the lowest $^4I_{15/2}$ state (i.e., 16×16 energy matrix), whereas the admixture between the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$ through crystal field interaction and those between $^4I_{15/2}$ (or $^4I_{13/2}$) state and the higher lying excited states with the same J value through spin-orbit (SO) coupling interaction are ignored and the comparisons between their theoretical results and the observed values were not given. In order to investigate the influence of the above ignored admixture effect between different energy levels to the EPR parameters, for similar trigonal $(ErO_6)^{9-}$ cluster in $Bi_4Ge_3O_{12}{:}Er^{3+}$ crystal, Bravo *et al.*[11] introduced the contributions of the first excited state $^4I_{13/2}$ state (i.e., 30×30 energy matrix) in the first-order perturbation treatment. However, the improvement by including $^4I_{13/2}$ state was very small. It seems that the significant improvement of theoretical results cannot be made within the limit of the first-order perturbation calculations and the second-order perturbation contributions arising from crystal field and orbital angular momentum interactions may be somewhat important, compared with the admixture effect between different energy levels. In order to check the contributions of the second-order terms and to study the EPR parameters and the local structures of the two different Er^{3+} centers in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals, we establish in this paper the perturbation formulas of EPR parameters $g_\parallel, g_\perp, A_\parallel$, and $A_\perp$ for the lowest Kramers doublet (Γ_6 or Γ_7) of $^4I_{15/2}$ of $4f^{11}$ ion in trigonal symmetry by considering the admixture between different energy levels and the second-order perturbation contributions. Based on these formulas, the EPR parameters of both Er^{3+} centers in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals are reasonably explained and their local structural parameters are also obtained. The results are discussed.

II. CALCULATION FORMULAS

When a $4f^{11}$ (Er^{3+}) ion enters the lattice of crystal, the cubic crystal field would split the ground state $^4I_{15/2}$ multiplet into two doublets Γ_6, Γ_7, and three Γ_8 quartets[12,13]. As the symmetry becomes lower (e.g., trigonal), the three Γ_8 representations may be split further into six doublets, whereas Γ_6 and Γ_7 remain unchanged and correspond to, respectively, the average EPR g values 6 and 6.8 to the first order in the absence of SO and admixture effects.[12,13]

In order to establish the perturbation formulas of Er^{3+} in trigonal symmetry, we should obtain the basis functions of Γ_6 or Γ_7 doublet by diagonalizing the energy matrix including the ground ${}^4I_{15/2}$ state. Considering that the first excited state ${}^4I_{13/2}$ is close to the ground ${}^4I_{15/2}$ state, the mixture between the two states via crystal field interaction would make contributions to the EPR parameters, the 30×30 matrix including both ${}^4I_{15/2}$ and ${}^4I_{13/2}$ states should be diagonalized to obtain the 15 groups (or irreducible representations) of basis functions in terms of the linear combination of $|JM_J\rangle$. Unlike the previous works,[9,12,13] the admixtures between ${}^4I_{15/2}$ and ${}^2K_{15/2}$, ${}^4I_{15/2}$ and ${}^2L_{15/2}$, and those between ${}^4I_{13/2}$ and ${}^2K_{13/2}$, ${}^4I_{13/2}$ and ${}^2I_{13/2}$ via SO coupling interaction are also included here. Thus, the basis functions for the lowest doublet Γ_6 or Γ_7 can be written as

$$\begin{aligned}|\Gamma\gamma^{(\gamma')}\rangle={}&\sum_{M_{J1}} C({}^4I_{15/2};\Gamma\gamma^{(\gamma')}M_{J1})N_{15/2}(|{}^4I_{15/2}M_{J1}\rangle\\&+\lambda_K|{}^2K_{15/2}M_{J1}\rangle+\lambda_L|{}^2L_{15/2}M_{J1}\rangle\\&+\sum_{M_{J2}} C({}^4I_{13/2};\Gamma\gamma^{(\gamma')}M_{J2})N_{13/2}(|{}^4I_{13/2}M_{J2}\rangle\\&+\lambda'_K|{}^2K_{13/2}M_{J2}\rangle+\lambda_I|{}^2L_{13/2}M_{J2}\rangle,\end{aligned}\tag{1}$$

where γ and γ' stand for the two components of Γ irreducible representation. M_{J1} and M_{J2} are in the range $-15/2$–$15/2$ and $-13/2$–$13/2$, respectively [note that the notations $\Gamma_6\alpha'(\beta')$ and $\Gamma_7\alpha''(\beta'')$ for $4f^{11}$ in cubic symmetry are still adopted here to indicate the lowest doublet for trigonal symmetry]. The mixing coefficients λ_i and normalization factors N_i in Eq. (1) can be determined by using SO coupling matrix elements and perturbation method.

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

$$\hat{H}'=\hat{H}_{\mathrm{CF}}+\hat{H}_Z+\hat{H}_{\mathrm{hf}}.\tag{2}$$

The crystal field interactions may be expressed in terms of Stevens equivalent operator under trigonal symmetry[12,13]

$$\hat{H}_{\mathrm{CF}}=B_2^0O_2^0+B_4^0O_4^0+B_4^3O_4^3+B_6^0O_6^0+B_6^3O_6^3+B_6^6O_6^6.\tag{3}$$

The Zeeman interaction $\hat{H}_z$ can be written as $\hat{H}_z=g_J\,\mu_B\,\mathbf{H}\cdot\hat{J}$, with their original meanings.[12,13] The hyperfine interaction $\hat{H}_{\mathrm{hf}}[=A_\parallel\hat{S}_Z\hat{I}_Z+(A_\perp/2)(\hat{S}_+\hat{I}_-+\hat{S}_-\hat{I}_+)]$ may be expressed in terms of the equivalent operator $\hat{N}$ of magnetic hyperfine structure as $\hat{H}_{\mathrm{hf}}=PN_J\hat{N}$, where N_J is the diagonal matrix element for ${}^{2S+1}L_J$ state and P the dipolar hyperfine structure constant in crystal.[12]

According to Ref. 12, the main contributions to EPR parameters may come from the first-order perturbation terms, however, the other $(15-1=14)$ irreducible representations Γ_x (i.e., six Γ_6 and eight Γ_7 for Γ_6 ground state, or seven Γ_6 and seven Γ_7 for Γ_7 ground state) would likely mix with the ground state (Γ_6 or Γ_7) via crystal field and orbital angular momentum (or hyperfine structure) interactions and so they make contributions to the EPR parameters [note that the second-order perturbation correction for $g_\perp$ (or $A_\perp$) vanishes because none of the Γ_x has nonzero matrix element with Γ ground state for both $\hat{H}_{\mathrm{CF}}$ and x or y component of $\hat{J}$ (or $\hat{N}$) operators, i.e., $g_\perp^{(2)}=A_\perp^{(2)}=0$]. Thus, by using the basis functions in Eq. (1) and perturbation Hamiltonian in Eq. (2), the second-order perturbation formulas of the EPR parameters $g_\parallel, g_\perp, A_\parallel$, and $A_\perp$ for the lowest Kramers doublet Γ_6 or Γ_7 can be derived as follows:

$$\begin{aligned}g_\parallel&=g_\parallel^{(1)}+g_\parallel^{(2)},\\g_\parallel^{(1)}&=2g_J\langle\Gamma\gamma|\hat{J}_Z|\Gamma\gamma\rangle,\\g_\parallel^{(2)}&=2\sum_X{}'\frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{L}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)},\\g_\perp&=g_\perp^{(1)}+g_\perp^{(2)},\\g_\perp^{(1)}&=2g_J\langle\Gamma\gamma|\hat{J}_X|\Gamma\gamma'\rangle,\\g_\perp^{(2)}&=0,\\A_\parallel&=A_\parallel^{(1)}+A_\parallel^{(2)},\\A_\parallel^{(1)}&=2PN_J\langle\Gamma\gamma|\hat{N}_Z|\Gamma\gamma\rangle,\\A_\parallel^{(2)}&=2\sum_X{}'\frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_Z|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)},\\A_\perp&=A_\perp^{(1)}+A_\perp^{(2)},\\A_\perp^{(1)}&=2PN_J\langle\Gamma\gamma|\hat{N}_X|\Gamma\gamma'\rangle,\\A_\perp^{(2)}&=0,\end{aligned}\tag{4}$$

where the parameters g_J, g'_J, N_J, and N'_J [note that g'_J and N'_J occur in the expansions of Eq. (4)] for various states are obtained from Refs. 12 and 13.

It should be noted that if only the first-order perturbation terms within the ${}^4I_{15/2}$ state are considered (i.e., all terms involve the excited states and second-order perturbation contributions vanish), Eq. (4) returns to the original results in the previous works.[9]

III. APPLICATIONS

Now we apply the above formulas to the calculations of two trigonal Er^{3+} defect centers in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals. (Note that the g factors of center II for Er^{3+} in MgO and ZnO codoped $LiNbO_3$ are the same within the experimental errors.[10] So, in the following studies, the same method and parameters are used for center II in both crystals.) The $LiNbO_3$ crystal structure belongs to the C_{3v}^6 space group, where Li^+ and Nb^{5+} cations occupy an octahedral site with C_3 (nearly C_{3v}) symmetry.[15,16] The disparture from C_{3v} symmetry is measured by the angle α of

TABLE I. EPR parameters $g_\parallel, g_\perp, A_\parallel$, and $A_\perp$ for the two trigonal Er^{3+} centers in $\mathrm{LiNbO_3}$ and MgO or ZnO codoped $\mathrm{LiNbO_3}$ crystals (where ''host'' and ''local'' stand for the calculations based on the host and local structural parameters, respectively).

	Center I					Center II				
	Cal.				Expt.	Cal.				Expt.
	Host	Local [a]	Local [b]	Local [c]		Host	Local [a]	Local [b]	Local [c]	
$g_\parallel$	13.89	12.85	13.63	15.12	15.14 [d] 15.14 (5) [e]	3.29	3.55	3.83	4.39	4.3 (2) [e] 4.26 (5) [e]
$g_\perp$	3.32	1.84	1.92	1.92	2.15 [d] 2.2 (9) [e]	8.19	7.22	7.83	7.83	7.6 (3) [e] 7.8 (1) [e]
$A_\parallel$ (10^{-4} cm^{-1})	520	463	514	571	70 [d]	109	130	147	160	
$A_\perp$ (10^{-4} cm^{-1})	104	66	72	72	70 [d]	285	249	282	282	

[a] Calculation by considering only the first-order perturbation terms within the $^4I_{15/2}$ state.

[b] Calculation by considering the admixtures between the ground state and the excited states but neglecting the second-order perturbation contributions.

[c] Calculation by considering the above admixtures and the second-order perturbation contributions.

[d] Ref. 9.

[e] Ref. 10.

the rotation of the upper (or equivalently the lower) oxygen triangle measured from one of the σ_v planes.[15] Since the angle α is very small (for Li^+ site, $\alpha \approx 3.82°$ and for Nb^{5+} site, $\alpha \approx 0.68°$, Refs. 15,16), it has been neglected in most crystal-field and EPR calculations for paramagnetic ions in $\mathrm{LiNbO_3}$[16,17] (it should be pointed out that a superposition model and crystal-field analysis of the $^4A_2$ and ^2_aE states of Cr^{3+} ion at C_3 rather than the approximate C_{3v} sites is made in Ref. 16, but the displacements of Cr^{3+} from the sites of the host ions were not considered). For simplicity, we apply C_{3v} approximation ($\alpha = 0$) here. Thus, the cation-anion bonding lengths and the angles between cation-anion bonds and C_3 axis in host $\mathrm{LiNbO_3}$ crystals are $R_1 \simeq 0.2238$ nm, $\theta_1 \simeq 44.57°$, $R_2 \simeq 0.2068$ nm, $\theta_2 \simeq 69.74°$ for Li^+ site, and $R_1 \simeq 0.1889$ nm, $\theta_1 \simeq 61.65°$, $R_2 \simeq 0.2112$ nm, $\theta_2 \simeq 47.99°$ for Nb^{5+} site, respectively.[15,16]

In order to calculate the crystal field parameters B_k^q in Eq. (3), the superposition model[18] is adopted, i.e.,

$$B_k^q = \sum_{j=1}^{n} \bar{A}_k(R_0) \left(\frac{R_0}{R_j} \right)^{t_k} K_k^q(\theta_j, \varphi_j), \tag{5}$$

where the coordination factor can be expressed by using the structural parameters of the studied system. $\bar{A}_k(R_0)$ and t_k are, respectively, the intrinsic parameters and the power law exponents. For the $(\mathrm{ErO_6})^{9-}$ clusters, the intrinsic parameters $\bar{A}_2(R_0) \simeq 1030$ cm^{-1}, $\bar{A}_4(R_0) \simeq 127.1$ cm^{-1}, $\bar{A}_6(R_0) \simeq 22.1$ cm^{-1} (with the reference distance $R_0 \simeq 0.21$ nm) and the power-law components $t_2 \simeq 3.4$, $t_4 \simeq 7.3$, and $t_6 \simeq 2.8$ were obtained for MgO:Er^{3+} crystal.[19] They can also be approximately applied in similar $(\mathrm{ErO_6})^{9-}$ clusters in $\mathrm{LiNbO_3}$:Er^{3+}.

Considering the covalency of Er^{3+}-O^{2-} bond in $\mathrm{LiNbO_3}$:Er^{3+} crystals, the orbital reduction factor $k \simeq 0.979$ is applied, as for similar $(\mathrm{ErO_6})^{9-}$ cluster in MgO:Er^{3+} crystal.[12] Thus, the SO coupling coefficient and dipolar hyperfine structure constant of Er^{3+} in $\mathrm{LiNbO_3}$ crystals can be obtained: $\zeta_{4f} \simeq k\zeta_{4f}^0$ (where $\zeta_{4f}^0 \simeq 2470$ cm^{-1}, the corresponding free ion value[12]) and $P \simeq kP_0$ (where $P_0 \simeq -54.6 \times 10^{-4}$ cm^{-1}, the free ion value[12]) owing to the covalency reduction effect. Similarly, the parameters of the Coulombic repulsion (i.e., $F^2 \simeq 97476$ cm^{-1}, $F^4 \simeq 70733$ cm^{-1}, $F^6 \simeq 47742$ cm^{-1}, Ref. 20) and two-body interaction terms (i.e., $\alpha \simeq 17$ cm^{-1}, $\beta \simeq -473$ cm^{-1}, $\gamma \simeq 1489$ cm^{-1}, Ref. 20) of free Er^{3+} ion may be multiplied with the factor k^2 to obtain the corresponding values for Er^{3+} ion in $\mathrm{LiNbO_3}$ crystals. Therefore, by using the SO matrix elements[21] and perturbation method, we have $\lambda_K \simeq -0.2020$, $\lambda_L \simeq 0.2359$, $N_{15/2} \simeq 0.9550$, $\lambda'_K \simeq -0.1080$, $\lambda_I \simeq 0.0464$, and $N_{13/2} \simeq 0.9932$.

According to the mean g values, it is agreed that for Er^{3+} centers I and II, the lowest doublets are, respectively, Γ_6 and Γ_7. If the host structural parameters R_i and θ_i for the Li^+ and Nb^{5+} sites in $\mathrm{LiNbO_3}$ are adopted, the trigonal crystal-field parameters can be calculated from Eq. (5). By applying these parameters B_k^q and the above other parameters to Eq. (4), the EPR parameters for both centers are calculated. The results are compared with the observed values in Table I.

From Table I, it can be found that for both Er^{3+} centers, the calculated EPR parameters, particularly, the anisotropies of g factors (characterized by $\Delta g = g_\parallel - g_\perp$) by adopting the host structural data are not consistent with the observed values, suggesting that the Er^{3+} ions in centers I and II do not occupy the exact Li^+ and Nb^{5+} sites, respectively. For center

TABLE II. The coefficients of state vectors in Eq. (1) in terms of $|JM_J\rangle$ based on the local structural parameters.

Center	$\|JM_J\rangle$	$\|\frac{15}{2},\pm\frac{13}{2}\rangle$	$\|\frac{15}{2},\pm\frac{7}{2}\rangle$	$\|\frac{15}{2},\pm\frac{1}{2}\rangle$	$\|\frac{15}{2},\mp\frac{5}{2}\rangle$	$\|\frac{15}{2},\mp\frac{11}{2}\rangle$
	$C(^4I_J;\Gamma_6\alpha'^{(\beta')}M_{J1})$	∓ 0.9085	± 0.3584	± 0.1342	± 0.1447	∓ 0.0790
$I(\Gamma_6)$	$\|JM_J\rangle$	$\|\frac{13}{2},\pm\frac{13}{2}\rangle$	$\|\frac{13}{2},\pm\frac{7}{2}\rangle$	$\|\frac{13}{2},\pm\frac{1}{2}\rangle$	$\|\frac{13}{2},\mp\frac{5}{2}\rangle$	$\|\frac{15}{2},\pm\frac{13}{2}\rangle$
	$C(^4I_J;\Gamma_6\alpha'^{(\beta')}M_{J1})$	± 0.0083	∓ 0.0126	0.0073	± 0.0088	∓ 0.0034
	$\|JM_J\rangle$	$\|\frac{15}{2},\pm\frac{13}{2}\rangle$	$\|\frac{15}{2},\pm\frac{7}{2}\rangle$	$\|\frac{15}{2},\pm\frac{1}{2}\rangle$	$\|\frac{15}{2},\mp\frac{5}{2}\rangle$	$\|\frac{15}{2},\mp\frac{11}{2}\rangle$
	$C(^4I_J;\Gamma_7\alpha''^{(\beta'')}M_{J1})$	-0.5031	0.2286	0.7693	0.1924	-0.2550
II(Γ_7)	$\|JM_J\rangle$	$\|\frac{13}{2},\pm\frac{13}{2}\rangle$	$\|\frac{13}{2},\pm\frac{7}{2}\rangle$	$\|\frac{13}{2},\pm\frac{1}{2}\rangle$	$\|\frac{13}{2},\mp\frac{5}{2}\rangle$	$\|\frac{15}{2},\pm\frac{13}{2}\rangle$
	$C(^4I_J;\Gamma_7\alpha''^{(\beta'')}M_{J1})$	± 0.0046	∓ 0.0142	0.0163	0.0082	0.0086

I, since the calculated Δg is smaller than the observed value, we can suggest that the Er^{3+} ion should be shifted away from the center of oxygen octahedron by an amount ΔZ_I along C_3 axis (the eccentric displacement of Er^{3+} ion in center I of $LiNbO_3:Er^{3+}$ was found by other experimental methods[22,23]) so that the trigonal distortion of Er^{3+} center I and hence the calculated anisotropy of g factor become larger. On the other hand, for center II, the larger calculated value of Δg than the observed value suggests that the Er^{3+} ion should be displaced towards the center of oxygen octahedron by ΔZ_{II} for reducing the trigonal distortion of $(ErO_6)^{9-}$ octahedron and hence the calculated Δg. By fitting the calculated EPR parameters to the observed values, we obtained the Er^{3+} displacements (note that the displacement direction towards the center of oxygen octahedron is defined as positive one) for both centers are

$$\Delta Z_{\mathrm{I}} \simeq -0.039\ \mathrm{nm}, \quad \Delta Z_{\mathrm{II}} \simeq 0.030\ \mathrm{nm}. \tag{6}$$

Obviously, the displacement directions of Er^{3+} in both centers are consistent with the suggestions based on the observed Δg. The corresponding crystal-field parameters can be calculated by using Eq. (5) and the local structural parameters in Eq. (6), i.e.,

$$B_2^0 \simeq -2308\ \mathrm{cm}^{-1}, \quad B_4^0 \simeq 1350\ \mathrm{cm}^{-1}, \quad B_6^0 \simeq -441\ \mathrm{cm}^{-1},$$
$$B_4^3 \simeq 1600\ \mathrm{cm}^{-1}, \quad B_6^3 \simeq -68\ \mathrm{cm}^{-1}, \quad B_6^6 \simeq 603\ \mathrm{cm}^{-1} \tag{7}$$

for center I and

$$B_2^0 \simeq 222\ \mathrm{cm}^{-1}, \quad B_4^0 \simeq -2533\ \mathrm{cm}^{-1}, \quad B_6^0 \simeq 423\ \mathrm{cm}^{-1},$$
$$B_4^3 \simeq 2812\ \mathrm{cm}^{-1}, \quad B_6^3 \simeq 201\ \mathrm{cm}^{-1}, \quad B_6^6 \simeq 349\ \mathrm{cm}^{-1} \tag{8}$$

for center II. Thus, the coefficients of the statevectors in Eq. (1) can be obtained and shown in Table II. The calculated EPR parameters (including the results using different approximate methods) are compared with the observed values in Table I. In addition, the calculated optical spectral data of the lowest $^4I_{15/2}$ state for both Er^{3+} centers in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals based on the local structural data are also comparable with the observed values (see Table III), suggesting that the parameters used in the above calculations are reasonable.

IV. DISCUSSIONS

(1) From Table II, it can be seen that for both Er^{3+} centers the calculated values of $g_\parallel$ and $g_\perp$ by considering all the contributions are in good agreement with the observed values. However, if the admixture effect between different energy levels and the second-order perturbation contribution are neglected, the agreements between calculation and experiment are not as good as those mentioned above. The improvement for $g_\parallel$ and $g_\perp$ by further considering the admixture effect between the ground state and excited state $^4I_{13/2}$ in the first-order perturbation scheme is about 6–8 %, whereas that for $g_\parallel$ by considering the second-order perturbation is about 12–14 %. The latter is about twice the former. So, in order to obtain the exact theoretical results of EPR parameters for Er^{3+} ion in crystals, the admixture effect between different energy levels as well as the second-order perturbation contribution should be taken into account.

(2) For center I, the calculated value of $A_\perp$ shows good agreement with the observed value, but that of $A_\parallel$ is significantly different from the observed value. Considering that the large trigonal distortion and hence the large anisotropy of

TABLE III. Optical spectra (in unit of cm^{-1}) of the lowest $^4I_{15/2}$ state for Er^{3+} centers I and II in $LiNbO_3$ and MgO or ZnO codoped $LiNbO_3$ crystals based on the local structural parameters.

Label		1	2	3	4	5	6	7
Center	Cal.	72	158	173	242	306	355	422
I	Expt.[a]	68	144	159	203	368	397	427
Center	Cal.	64	138	156	165	173	195	209
II	Expt.[b]	59	134	144	158	188	204	211

[a] Ref. 8.

[b] Ref. 24.

TABLE IV. g factors and hyperfine structure constants for Er^{3+} in various crystals.

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ ($10^{-4}\mathrm{cm}^{-1}$)	$A_{\perp}$ (10^{-4} cm^{-1})	References
$\mathrm{ThGeO_4:Er^{3+}}$	6.349	5.195	225	181	26
α-$\mathrm{LiIO_3:Er^{3+}}$	2.772 (3)	8.556 (3)	94.0 (3)	298 (1)	27
$\mathrm{Bi_4Ge_3O_{12}:Er^{3+}}$	9.6245 (5)	4.9570 (5)	335.2 (1)	171.9 (2)	11
$\mathrm{GaN:Er^{3+}}$	2.861 (3)	7.645 (3)	110 (5)	290 (5)	28
$\mathrm{ZnS:Er^{3+}}$	2.423 (4)	8.771 (5)	93 (10)	305 (1)	29
$\mathrm{YAsO_4:Er^{3+}}$	6.639 (2)	5.177 (4)	223 (1)	182 (1)	30
$\mathrm{YPO_4:Er^{3+}}$	6.42 (2)	4.81 (2)	214 (4)	163 (4)	30
$\mathrm{YVO_4:Er^{3+}}$	3.544 (5)	7.085 (5)	122.6 (4)	249.1 (8)	30
$\mathrm{ZrSiO_4:Er^{3+}}$	3.718 (2)	6.997 (6)	130.4 (6)	243.8 (11)	30

g factors for center I, the observed isotropy of hyperfine structure A [i.e., $A_{\parallel} \simeq A_{\perp} \simeq 70\times 10^{-4}$ cm^{-1} (Ref. 9)] is very astonishing. For Er^{3+} ion in crystals, the approximate relationship $g_{\parallel}/A_{\parallel} \simeq g_{\perp}/A_{\perp}$ was pointed out by some authors.[12,25] The relationship has been confirmed by the experimental EPR parameters for Er^{3+} in many crystals (see Table IV). The calculated EPR parameters for both Er^{3+} centers in $\mathrm{LiNbO_3}$ are consistent with the relationship. So, the observed value of $A_{\parallel}$ for center I in $\mathrm{LiNbO_3:Er^{3+}}$ is doubtful and remains to be further measured. For center II, no observed values of $A_{\parallel}$ and $A_{\perp}$ were reported. The above calculated values $A_{\parallel}$ and $A_{\perp}$ remain to be checked by the experimental studies.

(3) From the above studies, it is found that to reach the good fit between the calculated and experimental EPR parameters, the Er^{3+} ions in centers I and II do not occupy the exact Li^{+} and Nb^{5+} sites in $\mathrm{LiNbO_3}$, but are displaced away from the center of oxygen octahedron by about 0.039 nm for center I and towards the center of octahedron by about 0.030 nm for center II. For impurity ions in $\mathrm{LiNbO_3}$ crystal, an impurity displacement scheme was suggested in a previous paper,[31] i.e., the centers of oxygen octahedra along the c axis are occupied by cations in the sequence Li^{+},Nb^{5+} and a vacancy octahedron. The electrostatic repulsive forces between the neighboring Li^{+} and Nb^{5+} ions displace them from the centers of their octahedra, so that these cations are eccentric and close to the distinctive neighboring vacancies. If the cation is replaced by an impurity carrying extra charge compared with the replaced host ion, the repulsive force acting on the impurity should be greater and so the impurity should be shifted further away the center of octahedron. Whereas for the impurity having less charge than the replaced host ion, the displacement direction with respect to the center of octahedron is opposite (i.e., towards the center of octahedron) because the repulsive force decreases. From this scheme, the substitutional positions and impurity displacements for Fe^{3+} centers I and II in $\mathrm{LiNbO_3}$ and MgO codoped $\mathrm{LiNbO_3}$ crystals are obtained by analyzing their EPR data. The displacement ΔZ_{I} ($\simeq -0.004$ nm) for Fe^{3+} center I in sign and in magnitude is comparable with that ($\simeq -0.0058$ nm, Ref. 32) obtained by extended x-ray absorption fine structure (EXAFS) measurement (for Fe^{3+} center II, no observed value of impurity displacement was reported). In addition, the scheme is also supported by the following facts: for trivalent rare earth ions (Pr^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+}) replacing Li^{+} in $\mathrm{LiNbO_3}$ (center I), the Rutherford backscattering spectrometry (RBS)/channeling technique[23] and x-ray standing wave (XSW) measurement[22] showed that these impurities do not occupy exact Li^{+} site, but is shifted away from the center of oxygen octahedra by an amount ΔZ_{I} (the displacement in magnitude also depends upon the ionic radius of impurity, Ref. 23). Whereas for Cr^{3+} ion replacing Nb^{5+} site (center II), the electron nuclear double resonance (ENDOR) measurement[33] suggested that Cr^{3+} ion is displaced towards the center of oxygen octahedron by about 0.012 nm. So, the above impurity displacement scheme seems valid. Obviously, the displacement directions of both Er^{3+} centers in $\mathrm{LiNbO_3}$ and MgO or ZnO codoped $\mathrm{LiNbO_3}$ are consistent with the expectation based on this scheme. More importantly, for Er^{3+} center I, the Er^{3+} displacement ΔZ_I obtained in the present paper are close to the displacement ($\simeq -0.046$ nm, Ref. 22) obtained from XSW measurement and that ($\simeq -0.02$ nm, Ref. 23) measured by RBS/channeling technique (unfortunately, for Er^{3+} center II, no experimental result about impurity displacement was reported, the above calculated displacement remains to be checked by other experimental methods). So, the displacements for both Er^{3+} centers obtained in this paper can be regarded as reasonable. In passing, if we exchange the substitutional positions of Er^{3+} in both centers, i.e., Er^{3+} replaces Nb^{5+} in center I and Li^{+} in center II, by fitting the calculated EPR parameters to the observed values, the Er^{3+} displacement directions in both centers should be opposite to those in the above studies. These displacement directions are in disagreement with the expectation based on the above scheme (and the above experimental results for center I, Refs. 22,23) and cannot be regarded as suitable. So, the occupation positions of Er^{3+} in center I and II suggested in the previous papers and used in this paper are verified. It appears that some useful information about the substitutional position and defect structure for paramagnetic impurity in crystals can be obtained by analyzing the EPR parameters.

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