Studies on the Local Structure of the Tetragonal Er^{3+} Center in CaO

Shao-Yi Wu[a,b] and Hui-Ning Dong[b,c]

[a] Department of Applied Physics, University of Electronic Science & Technology of China,
Chengdu 610054, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016,
P. R. China
[c] College of Electronic Engineering, Chongqing University of Posts and Telecommunications,
Chongqing 400065, P. R. China

Reprint requests to S.-Y. W; E-mail: shaoyi-wu@163.com

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The local structure of the tetragonal Er^{3+} center in CaO is theoretically studied by using the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors from the second-order perturbation terms and the admixtures of various states are taken into account. Based on the investigations, this center is suggested to be the impurity Er^{3+} substituting the host Ca^{2+} site, associated with a Ca^{2+} vacancy V_{Ca} in the [100] (C_4) axis due to charge compensation. By studying the g factors of the tetragonal center, impurity Er^{3+} is expected to undergo an off-center displacement $\Delta Z (\approx 0.2$ Å) towards the V_{Ca} along the C_4 axis because of the electrostatic attraction. The calculated g factors based on the displacement ΔZ show reasonable agreement with the observed values.

Key words: Defect Structures; Electron Paramagnetic Resonance (EPR); Crystal-field and Spin Hamiltonians; Er^{3+}; CaO.

1. Introduction

CaO is an interesting material due to its geophysical interest [1 – 3] and applications in insulator coating [4, 5]. In addition, this material, when doped with rare-earth ions (such as Gd^{3+}, Eu^{2+}, Yb^{3+}, Dy^{3+} and Er^{3+}), has been studied by means of electron paramagnetic resonance (EPR) [6 – 9]. For example, the anisotropic g factors $g_{\parallel}$ and $g_{\perp}$ were measured for Er^{3+} doped CaO, which were attributed to a tetragonally distorted Er^{3+} center [9]. Until now, however, no quantitative investigations have been carried out on the above g factors, and the local structure of this tetragonal Er^{3+} center has not been determined, either.

In order to investigate theoretically the local structure of a tetragonal Er^{3+} center in CaO, which might be helpful to understand the properties of this material doped with Er^{3+}(or other rare-earth ions), in this paper, we study the local structure of this center by using the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors from the second-order perturbation theory and the admixtures of various energy levels are taken into account.

2. Calculations

When the impurity Er^{3+} is doped into the lattice of CaO, it may occupy an octahedral Ca^{2+} site due to its similar charge and size, with the extra positive charge compensated by one next-nearest-neighbouring cation vacancy V_{Ca} in the [100] (C_4) axis. As a result, the local symmetry is reduced from ideal cubic octahedral in

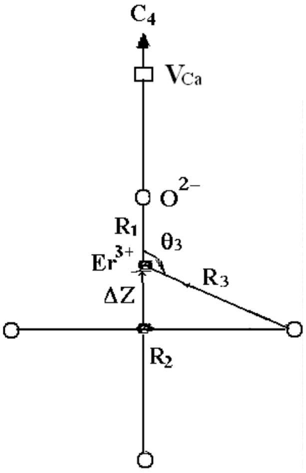

Fig. 1. Local structure of the tetragonal Er^{3+} center in CaO. The impurity Er^{3+} occupying the octahedral Ca^{2+} site may undergo an off-center displacement ΔZ towards the compensator vacancy V_{Ca} along the C_4 axis due to electrostatic attraction.

the pure crystal to a tetragonal (C_{4v}) in the Er^{3+} impurity center. Similar lattice distortions due to charge mismatching substitution are also mentioned for Cr^{3+} in MgO [10, 11] and V^{2+} in MCl (M = Na, K, Rb) crystals [12]. Because of the negative effective charge of the compensator V$_{\mathrm{Ca}}$ in the C$_4$ axis, the impurity Er^{3+} may shift towards it by an amount ΔZ along the C$_4$ axis due to the electrostatic attraction. Therefore, the local structure of this impurity center can be approximately described by the compensator V$_{\mathrm{Ca}}$ and the displacement ΔZ of the impurity Er^{3+} (see Fig. 1).

For an Er^{3+} (4f^{11}) ion in tetragonal crystal-fields, the ground state ^{4}I$_{15/2}$ would be split into eight Kramers doublets [13, 14]. The lowest doublet is Γ_6 or Γ_7, corresponding to the average value $\bar{g}$ [= $(g_{\parallel} + 2g_{\perp})/3$] of about 6 or 6.8, respectively [13, 14]. From the observed $\bar{g}$ ($\approx$ 6.82 [9]) for the studied Er^{3+} center in CaO, the lowest Kramers doublet should be assigned to Γ_7 doublet. As mentioned in our previous works [15, 16], in the studies of the g factors one may include the contributions due to the second-order perturbation terms, which originate from the admixtures between the lowest Γ_7 and the 14 irreducible representations Γ_x due to the tetragonal splitting of the ground state ^{4}I$_{15/2}$ and the first excited state ^{4}I$_{13/2}$ via the crystal-field $\hat{H}_{\mathrm{CF}}$ and the orbital angular momentum $\hat{J}$ interactions. Thus, the perturbation formulas of the g factors for a 4f^{11} ion in tetragonal symmetry can be expressed as [16]

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

$$\begin{aligned} g_{\perp} &= g_{\perp}{}^{(1)} + g_{\perp}{}^{(2)}, \\ g_{\perp}{}^{(1)} &= g_J\langle\Gamma\gamma|\hat{J}_+|\Gamma\gamma'\rangle, \quad g_{\perp}{}^{(2)} = 0. \end{aligned} \tag{2}$$

Here $\Gamma\gamma^{(\gamma')}$ (γ and γ' stand for the two components of the Γ irreducible representation) is the basic function of the lowest doublet. g_J are the Landé factors for various $^{2S+1}$L$_J$ configurations, which were given in [13, 14] [note: the nondiagonal elements g'_J may occur in the expansions of (1) and (2) due to the interactions between different $^{2S+1}$L$_J$ configurations]. The basic function $\Gamma\gamma^{(\gamma')}$ contains the admixtures of various states, i. e., the admixture between the ground state ^{4}I$_{15/2}$ and the excited state ^{4}I$_{13/2}$ via $\hat{H}_{\mathrm{CF}}$ interaction, the admixture among ^{2}K$_{15/2}$, ^{2}L$_{15/2}$, and ^{4}I$_{15/2}$ and that among ^{2}K$_{13/2}$, ^{2}I$_{13/2}$ and ^{4}I$_{13/2}$ via spin-orbit coupling interaction. Therefore, the formula of $\Gamma\gamma^{(\gamma')}$ may be written as [16]

$$\begin{aligned} |\Gamma\gamma^{(\gamma')}\rangle = &\sum_{M_{J1}} C(^4\mathrm{I}_{15/2};\Gamma\gamma^{(\gamma')}M_{J1})N_{15/2}(|^4\mathrm{I}_{15/2}M_{J1}\rangle + \lambda_{\mathrm{K}}|^2\mathrm{K}_{15/2}M_{J1}\rangle + \lambda_{\mathrm{L}}|^2\mathrm{L}_{15/2}M_{J1}\rangle) \\ &+ \sum_{M_{J2}} C(^4\mathrm{I}_{13/2};\Gamma\gamma^{(\gamma')}M_{J2})N_{13/2}(|^4\mathrm{I}_{13/2}M_{J2}\rangle + \lambda_{\mathrm{K}}'|^2\mathrm{K}_{13/2}M_{J2}\rangle + \lambda_{\mathrm{I}}|^2\mathrm{I}_{13/2}M_{J2}\rangle), \end{aligned} \tag{3}$$

where M_{J1} and M_{J2} are in the ranges of $-15/2$ to $15/2$ and $-13/2$ to $13/2$, respectively. The coefficients $C(^4\mathrm{I}_{15/2};\Gamma\gamma^{(\gamma')}M_{J1})$ or $C(^4\mathrm{I}_{13/2};\Gamma\gamma^{(\gamma')}M_{J2})$ can be determined by diagonalizing the 30×30 energy matrix including ^{4}I$_{15/2}$ and ^{4}I$_{13/2}$ states. λ_{i} and N_{i} are the mixing coefficients and the normalization factors. They can be determined from the spin-orbit coupling matrix elements and perturbation theory.

The crystal-field interaction $\hat{H}_{\mathrm{CF}}$ in the above formulas can be written in terms of the Stevens equivalent operators in tetragonal (C_{4v}) symmetry [13, 14]:

$$H_{\mathrm{CF}} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4. \tag{4}$$

The crystal-field parameters B_k^q ($k = 2, 4, 6; |q| \le k$) are determined from the superposition model (SPM) [17] and the local geometrical relationship of the studied impurity center, i. e.,

$$B_k^q = \sum_j \bar{A}_k K_k^q(\theta_j,\phi_j)(R_0/R_j)^{t_k}. \tag{5}$$

The coordination factors $K_k^q(\theta_j,\phi_j)(R_0/R_j)$ can be calculated from the local structural data of the studied system [17, 18]. $\bar{A}_k$ and t_k are the intrinsic parameters and the power-law exponents, respectively. R_0 is the reference distance. Since the charge and the ionic radius of the impurity Er^{3+} are different from those of the host Ca^{2+}, the reference distance (or the impurity-ligand distance) R_0 in the doped crystal may be unlike the host metal-ligand distance R_{H}. However, one can reasonably estimate the distance R_0 from the approximate relationship [19, 20]

$$R_0 \approx R_{\mathrm{H}} + (r_{\mathrm{i}} - r_{\mathrm{h}})/2, \tag{6}$$

Table 1. EPR g factors for the tetragonal Er^{3+} center in CaO.

	$g_{\parallel}$	$g_{\perp}$	$\Delta g\ (= g_{\perp} - g_{\parallel})$
Calc.	4.702	7.815	3.113
Expt. [9]	4.730 (5)	7.860 (10)	3.130 (15)

where r_i and r_h are the ionic radii of the impurity and the host ions, respectively. For the studied CaO:Er^{3+}, $r_i \approx 0.881$ Å, $r_h \approx 0.99$ Å [21] and $R_H \approx 2.405$ Å [21]. Then, we have $R_0 \approx 2.351$ Å. Since the local structure of the impurity center can be characterized by the displacement ΔZ, the local structural parameters (impurity-ligand bonding lengths R_j and angles θ_j) can be calculated from the distance R_0 and ΔZ by using the local geometrical relationship of the impurity center (see Fig. 1). For simplicity, we can define the O^{2-} in the positive direction of the C_4 axis as ligand 1, the one in the negative direction of the C_4 axis as ligand 2, and the other four planar O^{2-} as ligand 3. Thus, we have

$$R_1 \approx R_0 - \Delta Z, \quad R_2 \approx R_0 + \Delta Z, \quad R_3 \approx (R_0^2 + \Delta Z^2)^{1/2},$$
$$\theta_1 \approx 0, \quad \theta_2 \approx \pi, \quad \theta_3 \approx \pi/2 + \mathrm{tg}^{-1}(\Delta Z/R_0). \tag{7}$$

As regards the SPM parameters, the power-law exponents $t_2 \approx 3.4$, $t_4 \approx 7.3$, $t_6 \approx 2.8$ and the intrinsic parameters $\bar{A}_2 \approx 1030\ \mathrm{cm}^{-1}$, $\bar{A}_4 \approx 127.1\ \mathrm{cm}^{-1}$ and $\bar{A}_6 \approx 22.1\ \mathrm{cm}^{-1}$ for Er^{3+} in the similar MgO were obtained by SPM studies [22]. These parameters are approximately adopted here.

The free ion parameters of the Coulomb repulsion ($F^2 \approx 97{,}476\ \mathrm{cm}^{-1}$, $F^4 \approx 70{,}733\ \mathrm{cm}^{-1}$ and $F^6 \approx 47{,}742\ \mathrm{cm}^{-1}$), the two-body interaction parameters ($\alpha \approx 16.66\ \mathrm{cm}^{-1}$, $\beta \approx -473\ \mathrm{cm}^{-1}$ and $\gamma \approx 1489\ \mathrm{cm}^{-1}$) and the spin-orbit coupling coefficient ($\zeta_{4f} \approx 2345\ \mathrm{cm}^{-1}$) in the energy matrix were obtained [23]. Considering the admixture (or covalency) between the 4f orbitals of Er^{3+} and the 2p orbitals of O^{2-}, the orbital reduction factor $k (\approx 0.979)$ for similar MgO: Er^{3+} [13, 15] can also be adopted here.

Now, only the displacement ΔZ is unknown in the above formulas. Substituting these parameters into (1) and (2) and fitting the calculated g factors to the observed values, we obtain

$$\Delta Z \approx 0.2\ \text{Å}. \tag{8}$$

Note that the displacement direction towards the compensator is defined as positive. The corresponding theoretical g factors are compared with the observed values in Table 1.

3. Discussion

From Table 1, one can find that the theoretical g factors, particularly the anisotropy $\Delta g\ (= g_{\perp} - g_{\parallel})$, for the tetragonal Er^{3+} center in CaO based on the displacement ΔZ show reasonable agreement with the observed values. Thus, the local structure of this center is theoretically determined by analyzing its g factors.

(1) The large off-center displacement ΔZ (≈ 0.2 Å) obtained in the present work may contribute to the significant tetragonal distortion, which is characterized by the anisotropy Δg (≈ 3.130 [9]). Considering the strong electrostatic attraction between the trivalent Er^{3+} and the V_{Ca} (with two effective negative charges) due to charge compensation, the large displacement ΔZ can be understood. Interestingly, similar lattice distortions along the [100] (or C_4) axis were also reported for various octahedral clusters in MgO type crystals [10 – 12].

(2) There are some errors in the theoretical results. The errors of the impurity-ligand distance R_0 obtained from the empirical formula (6) would affect slightly the tetragonal distortion and the crystal-field parameters B_k^q, which depend largely upon the displacement ΔZ. If the host metal-ligand distance R_H is adopted, the estimated value for ΔZ would change by less than 5%. Meanwhile, the errors of adoption of the SPM parameters for MgO:Er^{3+} can also influence the calculated results. According to the theoretical analysis, the errors of the calculated g factors and the ΔZ are expected to be no more than 4% as the parameters $\bar{A}_k$ and t_k change by 10%.

(3) It is noted that the defect model (i. e., $[ErO_6]^{9-}$ cluster associated with one next-nearest-neighbouring V_{Ca} in the C_4 axis) established in this work may not be conclusive. First, the axial ligand "1" intervening in the Er^{3+} and the V_{Ca} would also shift away from the V_{Ca} by another amount $\Delta Z'$ due to the electrostatic repulsion of the compensator. This means that the actual bonding length R_1' in (7) would be further decreased by $\Delta Z'$, i.e., $R_1' \approx R_0 - \Delta Z - \Delta Z'$. Therefore, the large displacement ΔZ obtained in (8) should be regarded as the effective (or total) contributions to R_1 from both displacements. Second, the other five O^{2-} ligands may displace away from their ideal lattice sites because of the electrostatic repulsion of the V_{Ca}. Fortunately, in consideration of the less charge and the farther distances from the V_{Ca} for these O^{2-} than those for the Er^{3+}, their displacements may be much smaller than ΔZ. Furthermore, the shifting Er^{3+} would induce extra

electrostatic attraction upon these ligands, which may largely cancel the repulsion due to V_{Ca}. As a result, the displacements of the ligands and hence their influence on the calculated g factors and the shift ΔZ can be taken as negligible. Third, there may be other means of charge compensation for this tetragonal center. For example, the extra positive charge of Er^{3+} can be compensated with one of the next-nearest-neighbouring Ca^{2+} substituted by a monovalent ion, such as Li^+ and Na^+. This point is similar to the tetragonal Cr^{3+} center on Cd^{2+} site in Cs_2CdCl_4 [24]. So, the defect model and the local structure of this Er^{3+} center proposed here remains to be further checked with theoretical and experimental treatments.

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