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Investigations of the local structure and the g factors for the tetragonal Er^{3+} center in $KMgF_3$

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

[a]Department of Applied Physics, University of Electronic Science and 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

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Abstract

The local structure and the electron paramagnetic resonance (EPR) g factors for the tetragonal Er^{3+} center in $KMgF_3$ are 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 studies, the impurity Er^{3+} is expected to occupy the octahedral Mg^{2+} site, associated with an oxygen ion substituting for one of the nearest F^- (i.e., O_F) in the C_4 axis, due to charge compensation. Because of the electrostatic attraction of the compensator O_F, the Er^{3+} ion is found to take an axial displacement ΔZ (≈ 0.07 Å) towards the compensator along the C_4 axis. The calculated g factors based on the above displacement ΔZ show reasonable agreement with the observed values.

Keywords: Defects; Electron paramagnetic resonance (EPR); Crystal fields; Er^{3+}; $KMgF_3$

1. Introduction

$KMgF_3$ has been widely investigated due to the properties of dielectric characteristics, luminescence, green upconversion, laser action with proper dopants, and applications in fast position-sensitive registration systems [1–5]. Recently, this material doped with rare-earth ions (such as Er^{3+}, Ce^{3+}) has attracted extensive attentions because of thermoluminescence (TL), photoluminescence (PL), photoluminescence excitation (PLE), solid state laser and phosphors properties [6–11]. In general, these properties are relevant to local structures of doped rare-earth impurity ions. Since electron paramagnetic resonance (EPR) is a useful technique to study local structures of paramagnetic impurity centers in crystals, experiments have been carried out on Er^{3+}-doped $KMgF_3$ by means of the EPR technique. Abraham et. al. [12] found a tetragonal Er^{3+} center (as well as another two trigonal centers) in $KMgF_3$ and its g factors $g_{//}$ and $g_{\perp}$ were also measured by EPR experiment. This tetragonal Er^{3+} center was attributed to the impurity Er^{3+} occupying the octahedral Mg^{2+} site, associated with one substitutional O^{2-} ion at the original nearest F^- site (labeled as O_F) in the C_4 axis due to charge compensation [12].

Until now, however, no theoretical studies have been made on the above g factors, and the local structure of this tetragonal Er^{3+} center has not been determined, either. In order to verify theoretically the local structure of the tetragonal Er^{3+} center in $KMgF_3$, which may be useful to understand the properties of this material, and to make satisfactory interpretation to its g factors, we investigate in this paper the local structure and the g factors for the tetragonal Er^{3+} center in $KMgF_3$ from the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors arising from the second-order perturbation terms and the admixtures of various states are taken into account.

* Corresponding author. Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China.
E-mail address: wushaoyi@netease.com (S.-Y. Wu).

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2. Calculations

In general, rare earth ions (e.g., Ce^{3+}, Pr^{3+}, Eu^{2+}) preferentially substitute for K^+ in $KMgF_3$ [7,13–16], because they have similarly large radii (≈1.034, 1.013 and 1.09 Å [17]) comparable with that (≈1.33 Å [17]) of the replaced K^+. For Er^{3+}, however, the ionic radius (≈0.881 Å [17]) is much smaller and close to that (≈0.66 Å [17]) of Mg^{2+}. Thus, Er^{3+} can occupy both the dodecahedral K^+ and the octahedral Mg^{2+} sites and result in three different impurity centers, as pointed out in Ref. [12]. For the studied tetragonal center, Er^{3+} may locate on the octahedral Mg^{2+} site due to their similar size and charge, with the extra positive charge compensated by one nearest-neighbouring substitutional O_F in the C_4 axis [12]. As a result, the tetragonal (C_{4V}) Er^{3+} center, i.e., $[ErF_5O]^{4-}$ cluster, is formed. Because of the negative effective charge of the compensator O_F in the C_4 axis, the impurity Er^{3+} may shift towards the compensator by an amount ΔZ along the C_4 axis due to the electrostatic attraction. Therefore, the local structure of the impurity center can be approximately described by the compensator O_F and the displacement ΔZ of the impurity Er^{3+} (see Fig. 1).

For an $Er^{3+}(4f^{11})$ ion in tetragonal (C_{4V}) crystal-fields, the ground state $^4I_{15/2}$ would be split into eight Kramers doublets [18,19]. The lowest doublet is Γ_6 or Γ_7, corresponding to the average value $\bar{g}$ [$=(g_{//}+2g_{\perp})/3$] of about 6 or 6.8, respectively [18,19]. From the observed $\bar{g}$ (≈6.469 [12]) for the tetragonal Er^{3+} center in $KMgF_3$, the lowest Kramers doublet should be Γ_7. In the treatments of the previous works [18,19], merely the first-order perturbation contributions to the g factors were taken into account. In this work, however, we also include the contributions to the g factors arising from 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 $^4I_{15/2}$ and the first excited $^4I_{13/2}$ states via the crystal-field $\hat{H}_{CF}$ and the orbital angular momentum $\hat{J}$ interactions. Therefore, the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry can be expressed as [20]

$$g_{//} = g_{//}^{(1)} + g_{//}^{(2)},\ g_{//}^{(1)} = 2g_J < \Gamma\gamma|\hat{J}_z|\Gamma\gamma >,\ g_{//}^{(2)} = 2\sum_x{}' \frac{< \Gamma\gamma|\hat{H}_{CF}|\Gamma_x\gamma_x >< \Gamma_x\gamma_x|\hat{J}_z|\Gamma\gamma >}{E(\Gamma_x) - E(\Gamma)}, \quad (1)$$

$$g_{\perp} = g_{\perp}^{(1)} + g_{\perp}^{(2)},\ g_{\perp}^{(1)} = g_J < \Gamma\gamma|\hat{J}_+|\Gamma\gamma' >,\ g_{\perp}^{(2)} = 0. \quad (2)$$

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 Lande factors for various $^{2S+1}L_J$ configurations, which were given in Refs. [18,19] (note: the nondiagonal elements g_J' may occur in the expansions of Eqs. (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 $^4I_{15/2}$ and the excited $^4I_{13/2}$ states via $\hat{H}_{CF}$ interaction, the admixture among $^2K_{15/2}$, $^2L_{15/2}$, and $^4I_{15/2}$ and that among $^2K_{13/2}$, $^2I_{13/2}$ and $^4I_{13/2}$ via spin–orbit coupling interaction. Therefore, the formula of $\Gamma\gamma^{(\gamma)}$ may be written as [20]

$$\begin{aligned} |\Gamma\gamma^{(\gamma')} > \ = & \sum_{M_{J1}} C\left(^4I_{15/2}; \Gamma\gamma^{(\gamma')}M_{J1}\right)N_{15/2} \\ & \times \left(|^4I_{15/2}M_{J1} > + \lambda_K|^2K_{15/2}M_{J1} > \right. \\ & \left. + \lambda_L|^2L_{15/2}M_{J1} > \right) + \sum_{M_{J2}} C \\ & \times \left(^4I_{13/2}; \Gamma\gamma^{(\gamma')}M_{J2}\right)N_{13/2}\left(|^4I_{13/2}M_{J2} > \right. \\ & \left. + \lambda_{K'}|^2K_{13/2}M_{J2} > + \lambda_I|^2I_{13/2}M_{J2} > \right), \end{aligned} \quad (3)$$

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 $C\left(^4I_{15/2}; \Gamma\gamma^{(\gamma')}M_{J1}\right)$ or $C\left(^4I_{13/2}; \Gamma\gamma^{(\gamma')}M_{J2}\right)$ can be determined by diagonalizing the 30×30 energy matrix including $^4I_{15/2}$ and $^4I_{13/2}$ 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 method.

The crystal-field interaction $\hat{H}_{CF}$ in the above formulas can be written in terms of the Stevens equivalent operators in tetragonal (C_{4V}) symmetry [18,19]:

$$H_{CF} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4 \quad (4)$$

The crystal-field parameters B_k^q (k=2, 4, 6; $|q|\le k$) are determined from the superposition model (SPM) [21] and the local geometrical relationship of the studied impurity center, i.e.,

$$B_k^q = \sum_{j=1} \overline{A}_k(L_j)K_k^q(\theta_j, \phi_j)(R_0/R_j)^{t_k}. \quad (5)$$

The coordination factors K_k^q (θ_j,ϕ_j)can be calculated from the local structural data of the studied system

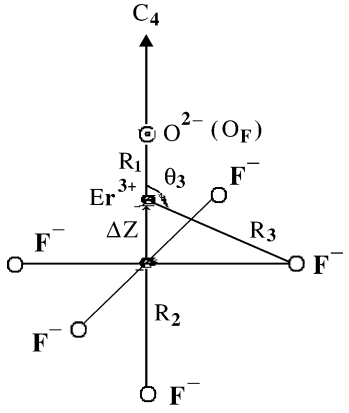

Fig. 1. Local structure of the tetragonal Er^{3+} center in $KMgF_3$. The impurity Er^{3+} occupying the octahedral Mg^{2+} site undergoes the axial displacement ΔZ towards the compensator O_F along the C_4 axis due to electrostatic attraction.