



A research on the g factors and defect model for the tetragonal Sm^{3+} center in KMgF_3 crystal

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ARTICLE INFO

Article history:

Received 7 November 2012

Received in revised form

5 February 2013

Accepted 14 March 2013

Available online 28 March 2013

Keywords:

Electron paramagnetic resonance

Defect structure

Crystal-field theory

KMgF_3

Sm^{3+}

ABSTRACT

The g factors g_{\parallel} and g_{\perp} for the tetragonal $(\text{SmF}_{12})^{9-}$ cluster due to Sm^{3+} occupying the 12-fold coordinated K^+ site in KMgF_3 perovskite are calculated from a diagonalization (of energy matrix) method. In the energy matrix, the crystal field parameters B_k^q used are calculated from the superposition model with the intrinsic parameters $\bar{A}_k(R_0)$ close to those of $(\text{GdF}_{12})^{9-}$ clusters for Gd^{3+} in similar cubic perovskite $c\text{-RbZnF}_3$. In the calculations, the applied defect model of tetragonal Sm^{3+} center in KMgF_3 is that in which Sm^{3+} occupies the 12-fold coordinated K^+ site associated with one (model A) or two (model B, where two K^+ vacancies are at both sides of Sm^{3+}) nearest K^+ vacancies along the C_4 axis for partial or complete charge compensation. The calculation results reveal that when the calculated g_{\parallel} and g_{\perp} are in reasonable agreement with the experimental values, the tetragonal distortions of Sm^{3+} centers are, whether in model A or model B, very small because of the slight anisotropy of the observed g factors. So, we suggest that the defect model of Sm^{3+} center is that in which Sm^{3+} occupies the 12-fold coordinated K^+ site associated with one or two next-nearest rather than nearest K^+ vacancies along the C_4 axis to result in small tetragonal distortions and hence in the small anisotropy of g factors. The reasonableness of our suggested defect model is discussed.

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1. Introduction

The cubic perovskite KMgF_3 crystals doped with rare earth (or $4f^n$) ions have been paid considerable attention due to their potential applications as UV tunable solid-state lasers, scintillators, dosimeters and phosphors [1–5]. Rare earth ions in KMgF_3 can occupy the cubic K^+ (12-fold coordination) and/or Mg^{2+} (6-fold coordination) cationic sites, depending upon the ionic radius of rare earth ion. Since the valence states of rare earth ions are often unlike those of the replaced host cations in KMgF_3 , the required charge compensators may frequently occur in the vicinity of rare earth impurity, resulting in the symmetry of impurity center being lower than the cubic. The properties of rare earth doped KMgF_3 crystals are connected to the defect model (including substitutional site, charge compensators and the symmetry of impurity center) and defect structure (i.e., the local lattice distortion) of rare earth impurity centers, so many spectroscopic experiments were carried out in order to study the defect model and defect structure of rare earth impurity centers [1,6–12]. Abdulsabirov et al. [12] measured the electron paramagnetic resonance (EPR) spectra for Sm^{3+} -doped KMgF_3 crystal and found a tetragonal Sm^{3+} center with g factors $g_{\parallel} \approx 0.574(1)$ and $g_{\perp} \approx 0.551(1)$ in KMgF_3 . By analyzing

the g factors, they [12] suggested that analogous to Ce^{3+} (I) ion [11], Sm^{3+} ion in KMgF_3 occupies the 12-fold coordinated K^+ site and the required charge compensation is provided by K^+ vacancies (V_K) nearest to Sm^{3+} and located on the C_4 axis. If the charge compensation is partial, only one V_K is nearest to Sm^{3+} (model A, see Fig. 1(a); this model was suggested for other trivalent rare earth ions in KMgF_3 [6] and similar cubic fluoroperovskite $c\text{-RbZnF}_3$ [13]), while if the compensation is complete, two V_K are nearest to Sm^{3+} (model B, see Fig. 1(b), Abdulsabirov et al. [12] suggested that the Sm^{3+} center belongs to model B). The defect model of the tetragonal Sm^{3+} center in KMgF_3 has not been further checked and its defect structure was not given. In this paper, we calculate the g factors of the tetragonal Sm^{3+} center in KMgF_3 based on the two defect models A and B from a diagonalization (of energy matrix) method. From the calculation, very small tetragonal distortions of Sm^{3+} center due to slight anisotropy of g factors are obtained and a new defect model is therefore suggested. The results are discussed.

2. Calculation

The electronic configuration of a free Sm^{3+} ion is $4f^5$ with the ground multiplet $^6\text{H}_{5/2}$. When Sm^{3+} occupies a tetragonal site in KMgF_3 , it undergoes a tetragonal crystal field which can split the ground multiplet $^6\text{H}_{5/2}$ into three Kramers doublets.

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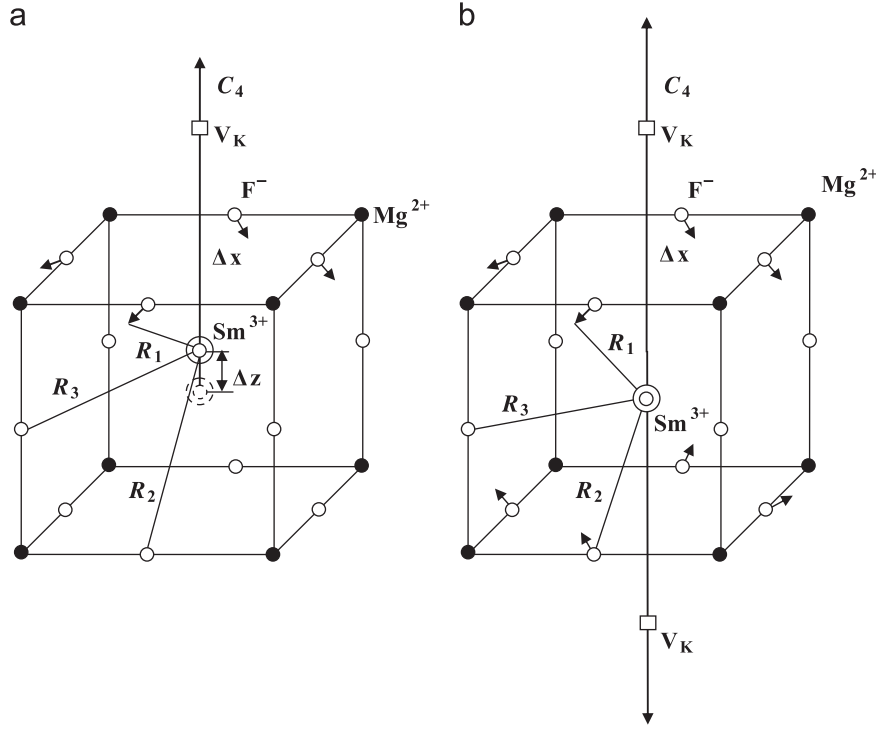


Fig. 1. The defect model of Sm^{3+} center in KMgF_3 crystal: (a) model A, similar to those in Refs. [6,13] or (b) model B, suggested in Ref. [12].

The measurement of g factor in EPR experiment needs an external magnetic field (which can split each Kramers doublet into two singlets). So, for the studies of g factors, the complete Hamiltonian of a $4f^n$ ion in crystal and under an external magnetic field H_M should take the form

$$H = H_f + H_{CF} + H_{Ze} \quad (1)$$

where H_f , H_{Ze} and H_{CF} are the free-ion, the Zeeman (or magnetic) interaction and crystal field interaction terms, respectively. They can be expressed as [14,15]

$$H_f = E_{AVE} + \sum_{k=2,4,6} F^k f_k + \zeta_{4f} A_{SO} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{t=2,3,4,6,7,8}^{k=2,4,6} t_i T_k + \sum_{k=0,2,4} m_k M^k + \sum_{k=2,4,6} p_k P^k \quad (2)$$

$$H_{Ze} = g_j \mu_B H_M \quad (3)$$

$$H_{CF} = B_2^0 C_2^0 + B_4^0 C_4^0 + B_4^4 (C_4^4 + C_4^{-4}) + B_6^0 C_6^0 + B_6^4 (C_6^4 + C_6^{-4}) \quad (4)$$

where the free-ion parameters in Eq. (2) are standard [14,15]. μ_B and g_j in Eq. (3) are the Bohr magneton and Lande factor, respectively. C_k^q and B_k^q in Eq. (4) are, respectively, the Racah spheric tensor operators and the crystal field parameters [14,15].

Since the influence of the high lying multiplets on the g factors of ground doublet is small [16], for simplicity, we establish the energy matrix of the above complete Hamiltonian in Eq. (1) considering only the ground multiplet ${}^6H_{5/2}$ and the first to fifth excited multiplets 6H_J (where $J=7/2, 9/2, 11/2, 13/2$ and $15/2$; note: these ground and excited multiplets have the same angular momentum $L=5$ and electron spin $S=5/2$). Thus, in terms of the irreducible tensors and/or equivalent operator methods, a 66×66 energy matrix for a $4f^7$ ion in tetragonal crystal field and under an external magnetic field H_M is obtained. The g factors can be calculated through diagonalizing the energy matrix by the

Table 1

The average free-ion parameters (in cm^{-1}) of Sm^{3+} ion [14].

F^2	F^4	F^6	α	β	γ	T^2	T^3	T^4	T^6
79012	56979	40078	20.50	-616	1565	282	26	71	-257
T^7	T^8	ζ_{4f}	M^0	M^2	M^4	P^2	P^4	P^6	
314	328	1170	2.38	1.33	0.90	336	252	168	

formulas

$$g_{\parallel} = g_z = \frac{\Delta E_{Ze}(z)}{\mu_B H_M}, \quad g_{\perp} = g_x = \frac{\Delta E_{Ze}(x)}{\mu_B H_M} \quad (5)$$

in which $\Delta E_{Ze}(i)$ ($i=x$ or z) represents the Zeeman splitting of ground Kramers doublet under an external magnetic field H_M along the i axis.

In the calculation, the free-ion parameters in Eq. (2) of Sm^{3+} ion are taken as the mean values obtained for Sm^{3+} ions in lots of crystals [14]. These free-ion values are listed in Table 1. For rare earth ions in crystals, the crystal field parameters B_k^q are frequently calculated from the empirical superposition model [17,18]. In the model, the parameter B_k^q is expressed as a sum of contributions from n ligands, i.e. [17,18]

$$B_k^q = \sum_{i=1}^n \bar{A}_k(R_0) \left(\frac{R_0}{R_i} \right)^{t_k} K_k^q(\theta_i, \varphi_i) / \alpha_{k_0} \quad (6)$$

where the coefficient α_{k_0} and the coordination factors $K_k^q(\theta_i, \varphi_i)$ depending upon the structure data of $4f^n$ centers are given in Ref. [17]. For the above tetragonal Sm^{3+} center in KMgF_3 , since the effective charge of V_K is negative, in model A the Sm^{3+} ion should shift toward V_K by Δz and the four F^- ions between Sm^{3+} and V_K should shift away from V_K along V_K-F^- direction by Δx [see Fig. 1(a)] owing to the electrostatic interaction, and in model B, from Fig. 1(b), the four F^- ions between Sm^{3+} and V_K in both above and below planes should shift away from the nearest V_K along V_K-F^- direction by Δx (and so $\Delta z=0$) because of electrostatic interaction. The defect

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