Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Physics and Chemistry of Solids 66 (2005) 109–114
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

Theoretical study of local crystal structure in $KZnF_3:Fe^{3+}$ system☆

Huang Xiao-Fen[a], Kuang Xiao-Yu[a,b,*], Lu Wei[a]

[a]*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*
[b]*International Centre for Materials Physics, Chinese Academy of Science, Shengyang 110016, China*

Received 29 March 2004; revised 9 August 2004; accepted 18 August 2004

Abstract

An analysis of the relationship between the EPR trigonal-field parameters and the local crystal structure of $KZnF_3:Fe^{3+}$ system is presented by diagonalizing the complete energy matrices for a d^5 configuration ion in a trigonal crystal field. We propose a two-layer-ligand model, in which the ligands consist of six nearest-neighbor F^- ions in the first layer and eight next nearest-neighbor K^+ ions in the second layer. The calculation indicates that the local structure distortion of $KZnF_3:Fe^{3+}$ system is due to the displacement of a K^+ ion along C_3 axis towards the Fe^{3+} ion, which leads to the shift of the F^- ions away from C_3 axis. By simulating the EPR low-symmetry parameters D and $(a-F)$, the distorted angles between the Fe^{3+}–F^- bonds and C_3 axis are determined, $\Delta\theta_1=2.58°$, $\Delta\theta_2=-1.4°$ at room temperature (300 K) and $\Delta\theta_1=2.84°$, $\Delta\theta_2=-1.4°$ at low temperature (77 K). Those results are in good agreement with the experimental findings $\Delta\theta_1=2.8\pm0.3°$and $\Delta\theta_2=-1.1\pm0.3°$.

1. Introduction

As a typical ionic crystal, the perovskite fluoride $KZnF_3$ doped with transition metal ions such as Fe^{3+}, Co^{2+}, Cr^{3+} has been studied experimentally and theoretically by many workers [1–5]. J.J. Krebs and R.K. Jeck's experiment [1] shows that when the Fe^{3+} ions dope into $KZnF_3$, the Fe^{3+} ion will substitute for the Zn^{2+} ion, and the local structure of $KZnF_3:Fe^{3+}$ is a cubic symmetry for the sufficiently low concentration of Fe^{3+} ($\leq$100 ppm) and a trigonal symmetry for the high concentration (>100 ppm). The ENDOR spectra indicate that the local trigonal distortion along the [111] direction (i.e. the C_3 axis) may be described by angles of deviation between the Fe^{3+}–F^- bonds and C_3 axis, by $\Delta\theta_1=2.8\pm0.3°$ and $\Delta\theta_1=-1.1\pm0.3°$, respectively. The EPR experiment, which also supports the trigonal distortion viewpoint, indicates that the spin Hamiltonian parameters of the Fe^{3+} ion in trigonal symmetry are $10^4a=45.6\ cm^{-1}$, $10^4D=103.4\ cm^{-1}$, $10^4(a-F)=49.5\ cm^{-1}$ at the room temperature ($T=300$ K) and $10^4a=49.7\ cm^{-1}$, $10^4D=107.9\ cm^{-1}$, $10^4\ (a-F)=52.4\ cm^{-1}$ at low temperature ($T=77$ K). J.J. Krebs and R.K. Jeck [1] speculated that in $KZnF_3:Fe^{3+}$ the trigonal distortion is due to the presence of a K^+ vacancy that is the next-nearest neighbor of the Fe^{3+} ion along [111] direction (or along the C_3 axis). Based on the V_k-model Yu [2] has studied the EPR parameters a, D and $(a-F)$ of the $KZnF_3:Fe^{3+}$ system using a high order perturbation procedure. His results indicated that the V_k-model cannot simultaneously explain the EPR low-symmetry second-order parameter D and fourth-order parameter $(a-F)$. In the present paper, the relationship between the local structure of the $KZnF_3:Fe^{3+}$ system and the EPR low-symmetry parameters D and $(a-F)$ will be studied using the diagonalization of the complete energy matrices. Our analysis will show that the two-layer-ligand model may satisfactorily explain both the local lattice distortion in $KZnF_3:Fe^{3+}$ and the EPR experimental data.

☆ This project was supported by National Natural Science Foundation of China.

* Corresponding author. Address: Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China.
E-mail address: zkwxx@263.net (K. Xiao-Yu).

0022-3697/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.jpcs.2004.08.035

2. Theoretical analyses

When the concentration of the doping Fe^{3+} ions in $KZnF_3$: Fe^{3+} is more than 100 ppm, the local structure of Fe^{3+} in $KZnF_3$:Fe^{3+} has C_{3v} symmetry [1]. The perturbation Hamiltonian for a d^5 configuration ion in trigonal symmetry can be written as

$$\hat{H} = \hat{H}_{ee} + \hat{H}_{so} + \hat{H}_{CF} = \sum_{i<j} e^2/r_{ij} + \zeta \sum_i l_i s_i + \sum_i V_i, \quad (1)$$

where the first term is the electron–electron interactions, the second term is the spin–orbit coupling interactions, and the third term is the ligand-field potentials, which can be expressed as

$$V_i = \gamma_{00} Z_{00} + \gamma_{20} r_i^2 Z_{20}(\theta_i, \varphi_i) + \gamma_{40} r_i^4 Z_{40}(\theta_i, \varphi_i) + \gamma_{43}^c r_i^4 Z_{43}^c(\theta_i, \varphi_i) + \gamma_{43}^s r_i^4 Z_{43}^s(\theta_i, \varphi_i), \quad (2)$$

According to the perturbation Hamiltonian (1), for a d^5 configuration ion two 84×84 energy matrices have been constructed in terms of the irreducible representations $\Gamma_4(\Gamma_5)$ and Γ_6 of C_3 point symmetry [6]. The matrix elements are functions of the Racah parameters B and C, the Trees correction α,the spin–orbit coupling coefficient ζ, and the crystal field parameters B_{20}, B_{40} and B_{43}^c [7], which are generally defined as [8]

$$B_{20} = \sum_\iota G_2(\tau) K_2^0(\tau), \; B_{40} = \sum_\iota G_4(\tau) K_4^0(\tau), \quad B_{43}^c = \frac{\sqrt{35}}{140} \sum_\iota G_4(\tau) K_4^3(\tau), \quad (3)$$

where

$$K_2^0(\tau) = \frac{1}{2}(3\cos^2\theta_\tau - 1), \quad K_4^0(\tau) = \frac{1}{8}(35\cos^4\theta_\tau - 30\cos^2\theta_\tau + 3), \quad K_4^3(\tau) = 35\cos\theta_\tau \sin^3\theta_\tau \cos 3\phi_\tau. \quad (4)$$

In Eqs. (3) and (4), τ represents the τth ligand, θ_τ, ϕ_τ represent the angular coordinates of the τth ligand. For the special case of the point-charge model, $G_2(\tau)$ and $G_4(\tau)$ may be written as

$$G_2(\tau) = eq_\tau G^2(\tau), \; G_4(\tau) = eq_\tau G^4(\tau), \quad (5)$$

where e and q_τ represent the charges of the electron and the τth ligand, respectively, and $G^k(\tau)$ ($k=2, 4$) are the integrals introduced by Gerloch and Slade [9]:

$$G^k(\tau) = \int_0^{R_\tau} R_{3d}^2(r) r^2 \frac{r^k}{R_\tau^{k+1}} \mathrm{d}r + \int_{R_\tau}^{\infty} R_{3d}^2(r) r^2 \frac{R_\tau}{r^{k+1}} \mathrm{d}r. \quad (6)$$

According to the Van Vleck approximation for $G^k(\tau)$ integral, we have

$$G_2(\tau) = \frac{eq_\tau \langle r^2 \rangle}{R_\tau^3}, \; G_4(\tau) = \frac{eq_\tau \langle r^4 \rangle}{R_\tau^5}, \; \frac{G_2(\tau)}{G_4(\tau)} = \frac{\langle r^2 \rangle}{\langle r^4 \rangle} R_\tau^2. \quad (7)$$

As long as we know the Racah parameters B and C, the Trees correction α, the spin–orbit coupling coefficient ζ, and the crystal field parameters B_{20}, B_{40}, B_{43}^c of Fe^{3+} in $KZnF_3$:Fe^{3+},the optical spectra and the ground-state splitting of the system can be calculated, and then the relationship between the EPR parameters and the local lattice structure of the $KZnF_3$:Fe^{3+} system can be further studied.

The EPR spectra of a d^5 configuration ion in trigonal symmetry may be analyzed by employing the spin Hamiltonian [10]:

$$\begin{aligned} \hat{H}_s = {} & g\beta \vec{H} \cdot \vec{S} + D[S_z^2 - S(S+1)/3] + a[S_\xi^4 + S_\eta^4 + S_\zeta^4 \\ & - S(S+1)(3S^2 + 3S - 1)/5]/6 \\ & + F[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) \\ & + 3S^2(2S+1)^2]/180, \end{aligned} \quad (8)$$

where a is the cubic-crystal-field splitting parameter, D and F correspond to the low-symmetry second- and fourth-order components. From Eq. (8) the splitting energy levels in the ground state $^6A_1$ for a zero-magnetic field can be written as

$$\begin{aligned} E\left(\pm\frac{1}{2}\right) &= D/3 - (a-F)/2 - [(18D + a - F)^2 + 80a^2]^{1/2}/6, \\ E\left(\pm\frac{3}{2}\right) &= -2D/3 + (a-F), \\ E\left(\pm\frac{5}{2}\right) &= D/3 - (a-F)/2 + [(18D + a - F)^2 + 80a^2]^{1/2}/6. \end{aligned} \quad (9)$$

Then the ground-state splitting ΔE_1 and ΔE_2 can be expressed as

$$\begin{aligned} \Delta E_1 &= E\left(\pm\frac{5}{2}\right) - E\left(\pm\frac{1}{2}\right) \\ &= \pm\frac{1}{3}[(a - F + 18D) + 80a^2]^{1/2}, \\ \Delta E_2 &= E\left(\pm\frac{3}{2}\right) - E\left(\pm\frac{1}{2}\right) \\ &= \frac{3}{2}(a - F) - D \pm \frac{1}{6}[(a - F + 18D)^2 + 80a^2]^{1/2}, \end{aligned} \quad (10)$$

where the signs '+' and '−' correspond to $D \geq 0$ and $D < 0$, respectively. Kuang has shown that the low-symmetry EPR parameters D and $(a-F)$ are almost independent of the cubic EPR parameter a for Fe^{3+} in Al_2O_3 [6]. We note that this conclusion is also suitable for the $KZnF_3$:Fe^{3+} system, so we can take an cubic approximation in the calculation of the EPR parameter a and determine D and $(a-F)$ by using Eq. (10) as well as the corresponding values ΔE_1, ΔE_2 from the diagonalization of the complete energy matrices.

Based on the two different models, one with a K^+ vacancy and the other without a K^+ vacancy, we will, respectively, study the relationship between the EPR