

# Local molecular structure and thermal expansion coefficient for octahedral $\text{Fe}^{3+}$ center in $\text{AlF}_3:\text{Fe}^{3+}$ system

Ju-Fen Li<sup>a</sup>, Xiao-Yu Kuang<sup>a,b,\*</sup>, Ai-Jie Mao<sup>a</sup>, Hui Wang<sup>a</sup>

<sup>a</sup> Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

<sup>b</sup> International Centre for Materials Physics, Chinese Academy of Science, Shenyang 110016, China

Received 1 November 2006; received in revised form 10 December 2006; accepted 9 February 2007

Available online 16 February 2007

## Abstract

A theoretical method for studying the inter-relation between electronic and molecular structure has been proposed by diagonalizing the complete energy matrices for  $d^5$  configuration ion in a trigonal ligand-field. Based on this method, the local lattice distortion of  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system ( $\text{AlF}_3$  is the component of fluoride glasses or is the single crystal) has been studied by considering the second-order and fourth-order EPR parameters  $D$  and  $(a - F)$ , simultaneously. The results indicate that the local lattice structure around octahedral  $\text{Fe}^{3+}$  center has an expansion distortion whether  $\text{AlF}_3:\text{Fe}^{3+}$  is the component of fluoride glasses or  $\text{Fe}^{3+}$  is doped in the  $\text{AlF}_3$  single crystal. The expansion distortion may be ascribed to the fact that the radius of  $\text{Fe}^{3+}$  ion is larger than that of  $\text{Al}^{3+}$  ion, and the  $\text{Fe}^{3+}$  ion will push the fluoride ligand outwards, respectively. Furthermore, the thermal expansion coefficient of  $\text{Fe}^{3+}$  in the single crystal  $\text{AlF}_3:\text{Fe}^{3+}$  depending on the temperature are reported and some characteristics of it are also analyzed.

© 2007 Published by Elsevier B.V.

PACS: 71.70.Gm; 75.30.Et; 71.70.Ch

Keywords:  $\text{AlF}_3:\text{Fe}^{3+}$  system; Local lattice structure distortion; EPR spectrum; Ligand-fields theory; Thermal expansion coefficient

## 1. Introduction

The transition-metal cluster may display various spin ground states, such as high-spin, low-spin, or intermediate-spin states, depending on the relative strength of the ligand-field energy and the mean spin-pairing energy [1–10]. In order to describe the various characteristics of transition-metal cluster, it is important to establish the relation between electronic and molecular structure. In the present work, a theoretical method for determining the relation for a  $d^5$  configuration ion in a trigonal ligand-field is proposed by diagonalizing the complete energy matrices and simulating the second-order and fourth-order EPR parameters  $D$  and  $(a - F)$ , simultaneously. Using this method, the local lattice distortion for  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system ( $\text{AlF}_3$  is the component of fluoride glasses or the single crystals), as well as the thermal expansion coefficient for  $\text{Fe}^{3+}$  doped in the single crystals  $\text{AlF}_3$  are studied, respectively.

Fluoride glasses have emerged as the material of choice for optical fiber amplifiers and fiber lasers and quickly became a major interest for telecommunication application [11–14].  $\text{AlF}_3$  as the component in the fluoride glasses, it become more and more important. Especially, metal fluoride glasses based of  $\text{AlF}_3$ ,  $\text{ZnF}_2$ ,  $\text{InF}_3$  etc., which present a high optical transparency in the mid infrared, have been extensively applied in optical sensors, fiber laser, optical amplifiers, optical fibers [15–17] etc. Nowadays, it is important and interesting thing to investigate the compound and local lattice distortion structure of fluoride glasses by EPR using  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  probes. Thus, the detailed knowledge of the impurity in  $\text{AlF}_3$  by transition-metal ions is prerequisite for complete understanding of the electrical and optical properties of all kinds of fluoride glasses. Electron paramagnetic resonance (EPR) is an effective method to study the local geometry and local properties in the vicinity of impurity. The single crystal  $\text{AlF}_3:\text{Fe}^{3+}$  and  $\text{AlF}_3:\text{Cr}^{3+}$  in the fluoride glasses have been investigated in recent years [18–21]. Scholz et al. [21] and Legein et al. [20] have studied single crystals  $\text{AlF}_3$  and the transition-metal fluoride glasses by EPR using  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  as local probes, respectively. Both Scholz et al. and Legein

\* Corresponding author.

E-mail address: scu\_kxy@163.com (X.-Y. Kuang).

et al. found that the  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system has a trigonal distortion whether in the fluoride glasses or the single crystal. In the Scholz's work, they have observed the EPR spectra of single crystal  $\text{AlF}_3$  depending on the temperature, and their conclusion is that the  $\text{Fe}^{3+}$  will replace  $\text{Al}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system [21]. As for the Legein's work, they have found that the  $\text{Fe}^{3+}$  in the  $\text{AlF}_3:\text{Fe}^{3+}$  system ( $\text{AlF}_3$  is the component of fluoride glasses) has a trigonal distortion [20]. The observed EPR parameters,  $10^4 b_2^0 = 165 \text{ cm}^{-1}$ ,  $10^4 b_4^0 = -12.5 \text{ cm}^{-1}$ ,  $10^4 b_4^3 = 325 \text{ cm}^{-1}$  for  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system are ascribed to the trigonal distortion along [1 1 1] direction. Legein et al. have analyzed the trigonal distortion based on the EPR parameter  $D$  with superposition model [20]. It is well known that for a  $d^5$  configuration ion in a trigonal ligand-field, the high-spin ground state is the  ${}^6A_1$  state. To reproduce the  ${}^6A_1$  ground state splitting of  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system, generally, the spin Hamiltonian should include  $a$  and  $(a - F)$ , besides  $D$  [22]. Parameter  $a$  is associated with a fourth-order spin operator and represents a cubic component of the crystalline electric field. Parameters  $D$  and  $(a - F)$  are, respectively, associated with the second-order and fourth-order spin operators and represent a component of the crystalline electric field that is axially symmetric about the  $C_3$  axis. Since both the EPR parameters  $D$  and  $(a - F)$  relate to the axial ligand-field, herein, we will suggest that the parameters  $D$  and  $(a - F)$  should be simultaneously considered in the determination of the local distortion structure of  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system ( $\text{AlF}_3$  is the component of the fluoride glasses or single crystal). Based on all above points, in present work, we will study the EPR parameters  $a$ ,  $D$  and  $(a - F)$  of  $\text{Fe}^{3+}$  in  $\text{AlF}_3:\text{Fe}^{3+}$  system ( $\text{AlF}_3$  is the component of the fluoride glasses or single crystal) simultaneously by diagonalizing the complete energy matrices for a  $d^5$  configuration ion in a trigonal crystal field.

## 2. Energy matrix and EPR parameter in a trigonal ligand-field

For the  $\text{AlF}_3:\text{Fe}^{3+}$  system, the EPR spectrum of trigonal  $\text{Fe}^{3+}$  ( $S=5/2$ ) center has been described by means of the following spin Hamiltonian [19,20]:

$$\hat{H}_S = g_{\parallel} \beta S_{\zeta} H_{\zeta} + g_{\perp} \beta (S_{\xi} H_{\xi} + S_{\eta} H_{\eta}) + \left(\frac{1}{3}\right) b_2^0 O_2^0 + \left(\frac{1}{60}\right) (b_4^0 O_4^0 + b_4^3 O_4^3) \quad (1)$$

where  $O_n^m$  are the standard Stevens spin operators and  $b_n^m$  are zero-field splitting parameters. From the spin Hamiltonian, the splitting energy levels in the ground state  ${}^6A_1$  for a zero magnetic field are given as follows:

$$\begin{aligned} E_{\pm 1/2} &= \left(\frac{1}{3}\right) b_2^0 + \left(\frac{3}{2}\right) b_4^0 \mp \left(\frac{1}{6}\right) [(18b_2^0 - 3b_4^0)^2 + \left(\frac{9}{10}\right) (b_4^3)^2]^{1/2}, \\ E_{\pm 3/2} &= -\left(\frac{2}{3}\right) b_2^0 - 3b_4^0, \\ E_{\pm 5/2} &= \left(\frac{1}{3}\right) b_2^0 + \left(\frac{3}{2}\right) b_4^0 \pm \left(\frac{1}{6}\right) [(18b_2^0 - 3b_4^0)^2 + \left(\frac{9}{10}\right) (b_4^3)^2]^{1/2}. \end{aligned} \quad (2)$$

Herein, the upper signs and lower signs of “ $\pm$ ” and “ $\mp$ ” in Eq. (2) correspond to  $b_2^0 \geq 0$  and  $b_2^0 < 0$ , respectively.

Then, the zero-field splitting energies,  $\Delta E_1$  and  $\Delta E_2$ , in the ground  ${}^6A_1$  state can be explicitly expressed as a function of the EPR parameters  $b_2^0$ ,  $b_4^0$  and  $b_4^3$

$$\begin{aligned} \Delta E_1 &= \left(\pm \frac{1}{3}\right) [(18b_2^0 - 3b_4^0)^2 + \left(\frac{9}{10}\right) (b_4^3)^2]^{1/2}, \\ \Delta E_2 &= -b_2^0 - \left(\frac{9}{2}\right) b_4^0 \pm \left(\frac{1}{6}\right) [(18b_2^0 - 3b_4^0)^2 + \left(\frac{9}{10}\right) (b_4^3)^2]^{1/2}. \end{aligned} \quad (3)$$

The positive and negative signs in Eq. (3) correspond to  $b_2^0 \geq 0$  and  $b_2^0 < 0$ , respectively, where  $b_n^m$  are zero-field splitting parameters. The simple relation between  $b_n^m$  and the EPR parameters  $a$ ,  $D$  and  $(a - F)$  may be written

$$b_2^0 = D, \quad b_4^0 = -\frac{a - F}{3}, \quad b_4^3 = -20 \frac{\sqrt{2}}{3} a \quad (4)$$

According to Eqs. (4) and (2), the zero-field splitting energies,  $\Delta E_1$  and  $\Delta E_2$ , in the ground  ${}^6A_1$  state can also be explicitly expressed as a function of the EPR parameters  $a$ ,  $D$  and  $(a - F)$

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

The perturbation Hamiltonian for a  $d^5$  configuration ion in trigonal symmetry can be written as

$$\begin{aligned} \hat{H} &= \hat{H}_{ee} + \hat{H}_{so} + \hat{H}_{lf} \\ &= \sum_{i < j} \frac{e^2}{r_{i,j}} + \zeta \sum_i l_i \cdot s_i + \sum_i V_i, \end{aligned} \quad (6)$$

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 potential, which can be expressed as

$$\begin{aligned} V_i &= \gamma_{00} Z_{00} + \gamma_{20} r_i^2 Z_{20}(\theta_i, \varphi_i) + \gamma_{40} r_i^4 Z_{40}(\theta_i, \varphi_i) \\ &\quad + \gamma_{43}^c r_i^4 Z_{43}^c(\theta_i, \varphi_i) + \gamma_{43}^s r_i^4 Z_{43}^s(\theta_i, \varphi_i), \end{aligned} \quad (7)$$

where  $r_i$ ,  $\theta_i$  and  $\varphi_i$  are spherical coordinates of the  $i$ th electron.  $Z_{lm}$ ,  $Z_{lm}^c$  and  $Z_{lm}^s$  are defined as

$$\begin{aligned} Z_{l0} &= Y_{l0}, \\ Z_{lm}^c &= \left(\frac{1}{\sqrt{2}}\right) [Y_{l,-m} + (-1)^m Y_{l,m}], \\ Z_{lm}^s &= \left(\frac{i}{\sqrt{2}}\right) [Y_{l,-m} + (-1)^m Y_{l,m}], \end{aligned} \quad (8)$$

the  $Y_{l,m}$  in Eq. (8) are the spherical harmonics.  $\gamma_{l0}$ ,  $\gamma_{lm}^c$  and  $\gamma_{lm}^s$  are associated with the local lattice structure around  $d^5$

Download English Version:

<https://daneshyari.com/en/article/1624265>

Download Persian Version:

<https://daneshyari.com/article/1624265>

[Daneshyari.com](https://daneshyari.com)