



# Zero-field splitting of the ground state and local lattice distortions for $\text{Fe}^{3+}$ ions at the tetragonal $\text{FeF}_5\text{O}$ cluster center in $\text{Fe}^{3+}:\text{KMgF}_3$ crystals

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## ABSTRACT

The relations between the zero-field splitting (ZFS) parameters and the structural parameters of the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals have been established by means of the microscopic spin Hamiltonian theory and the superposition model (SPM). On the basis of this, the local structure distortions, the second-order ZFS parameter  $D$ , the fourth-order one ( $a + 2F/3$ ), and the energy level separations  $\Delta_1$  and  $\Delta_2$  of the ground spin state for  $\text{Fe}^{3+}$  ion doped in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals are theoretically investigated. We use complete diagonalization method (CDM) and take into account the electronic magnetic interactions, i.e. the spin-spin (SS), the spin-other-orbit (SOO), and the orbit-orbit (OO) interactions, besides the well-known spin-orbit (SO) interaction. This investigation reveals that the replacement of  $\text{O}^{2-}$  for  $\text{F}^-$  and the induced lattice relaxation  $\Delta R_2(\text{O})$ , combined with an inward relaxation of the nearest five fluorine ions  $\Delta R_1(\text{F})$  give rise to a strong tetragonal crystal field, which yields the large ZFS of the ground state. The theoretically calculated parameters  $D$ , ( $a + 2F/3$ ),  $\Delta_1$ , and  $\Delta_2$  for  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals are in good agreement with experimental ones when the five  $\text{F}^-$  ions move toward  $\text{Fe}^{3+}$  by  $|\Delta R_1(\text{F})| = 6.40 \times 10^{-4}$  nm and the  $\text{O}^{2-}$  ion toward  $\text{Fe}^{3+}$  by  $|\Delta R_2(\text{O})| = 10.55 \times 10^{-3}$  nm.

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## 1. Introduction

The perovskite fluorides  $\text{AMF}_3$  (A represents an alkali metal and M an alkaline-earth metal ion) crystal exhibits a range of useful physical and chemical properties, including the ferromagnetic, photoluminescent and photoelectric properties [1–4]. In particular,  $\text{KMgF}_3$  crystals doped with transition-metal (TM) ions, e.g.  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{3+}$  have attracted much attention due to their potential applications in laser technologies [5–9], which depend strongly on the presence of defects induced by the transition metal impurities.  $\text{KMgF}_3$  crystals have cubic structure, the  $\text{Mg}^{2+}$  ion is surrounded by six  $\text{F}^-$  ion in a regular octahedron [10]. Trivalent dopant  $\text{Fe}^{3+}$  ions replace divalent  $\text{Mg}^{2+}$  ions in  $\text{KMgF}_3$ . However, the electron paramagnetic resonance (EPR) and electron-nuclear double-resonance (ENDOR) experiments on  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals [10,11] show that the  $\text{Fe}^{3+}$  ions are located at tetragonal symmetry sites.  $\text{Fe}^{3+}$  ions exhibit very large rank-2 zero-field splitting (ZFS) parameter  $D = -35.2 \times 10^{-2} \text{ cm}^{-1}$  [11], much is several times greater than for the M-vacancy tetragonal  $\text{Fe}^{3+}$  sites in  $\text{AMF}_3$  crystals:  $D = 7.40 \times 10^{-2} \text{ cm}^{-1}$  for  $\text{Fe}^{3+}:\text{KZnF}_3$  [12],  $D = -4.22 \times 10^{-2} \text{ cm}^{-1}$  for  $\text{Fe}^{3+}:\text{RbCdF}_3$  [8], and  $D = -5.48 \times 10^{-2} \text{ cm}^{-1}$  for  $\text{Fe}^{3+}:\text{CsCdF}_3$  [8]. This result implies that the local structure of  $\text{Fe}^{3+}$  in  $\text{Fe}^{3+}:\text{KMgF}_3$

crystal experiences tetragonal distortion reducing the local symmetry around  $\text{Fe}^{3+}$  ion from  $\text{O}_h$  to  $\text{C}_{4v}$ . Analysis of the nearest-neighbor  $\text{F}^-$  superhyperfine structure patterns for  $\text{Fe}^{3+}$  in  $\text{KMgF}_3$  [10] shows that only five of the nearest-neighbor fluorine ions were presented, with the sixth site being occupied by a negatively divalent ions with zero nuclear spin such as  $\text{O}^{2-}$ . Thus the large ZFS parameter  $D$  has been attributed to  $\text{Fe}^{3+}$  ions at tetragonal sites with  $\text{O}^{2-}$  ions on the tetragonal axis, i.e. tetragonal  $\text{FeF}_5\text{O}$  cluster center [10].

Since TM impurity ions are responsible for the modification of the materials properties, the understanding of the local structure and the fine structure of the ground state for  $\text{Fe}^{3+}$  ions in  $\text{KMgF}_3$  crystals is important. However, such studies are lacking. In order to understand the role of magnetic ion on a microscopic scale and gain quantitative knowledge about the effects of the surrounding ions, it is necessary to study the defect nature and local structure distortions of the impurity centers. The ZFS parameters obtained from the EPR experiments in crystals are useful for this purpose since they reflect very sensitively even small variations in the coordination of the paramagnetic centers [13–15]. Hence, the studies of ZFS parameters can provide a great deal of microscopic insight concerning the crystal structure, structural disorder as well as the observed magnetic and spectroscopic properties [16–18]. In this work, the relationship between the ZFS parameters and the local structure of the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals is established based on the superposition model [19,20] and the microscopic spin Hamiltonian theory [21–23]. By simulating the rank-2 ZFS parameter  $D$  and

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the rank-4 ZFS parameter ( $a + 2F/3$ ) as well as the fine structure of the ground state of  $\text{Fe}^{3+}$  in  $\text{KMgF}_3$  simultaneously, the local structure distortion of this  $\text{Fe}^{3+}$  center is investigated using complete diagonalization method (CDM) [24,25]. Our results show that the replacement of  $\text{O}^{2-}$  for  $\text{F}^-$  and the induced lattice relaxation, combined with an inward relaxation of the nearest five fluorine ions give rise to a strong tetragonal crystal field, which yields the large ZFS of the ground state.

## 2. Theoretical analysis

The present work utilizes the CFA/MSH package based on the complete diagonalization method (CDM) [14,15,26] for the  $3d^5$  ions at tetragonal symmetry CF. The *physical* Hamiltonian for  $\text{Fe}^{3+}$  ion in tetragonal symmetry CF is given as [15]

$$H = H_{\text{ee}}(B, C) + H_{\text{CF}}(B_{\text{kq}}) + H_{\text{m}}(\xi_{\text{d}}, M_0, M_2) \quad (1)$$

where the first term represents the Coulomb interactions, the second – CF Hamiltonian:

$$H_{\text{CF}} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}(C_4^{(4)} + C_{-4}^{(4)}) \quad (2)$$

where the  $C_q^{(k)}$  are normalized spherical harmonics. For the tetragonal symmetry ( $z//C_4$ ). It is convenient to define [27,28]

$$B_{20} = \delta - \mu \quad (3a)$$

$$B_{40} = 21Dq - \frac{3}{5}(3\mu + 4\delta) \quad (3b)$$

$$B_{44} = 21\sqrt{\frac{5}{14}}Dq \quad (3c)$$

where  $Dq$  is the cubic CF parameter, whereas the parameters  $\mu$  and  $\delta$  [29] measure the net tetragonal CF components and vanish identically in cubic site. Thus the parameters  $\mu$  and  $\delta$  altogether can characterize the tetragonal distortion effect reducing the local symmetry around  $\text{Fe}^{3+}$  from  $\text{O}_h$  to  $\text{C}_{4v}$  for  $\text{Fe}^{3+}$  in  $\text{KMgF}_3$ . The last term in Eq. (1) represents the magnetic interactions including apart from the SO interaction, also the spin-other-orbit (SOO), the spin–spin (SS), and the orbit–orbit (OO) interactions:

$$H_{\text{m}} = H_{\text{so}}(\xi_{\text{d}}) + H_{\text{soo}}(M_0, M_2) + H_{\text{ss}}(M_0, M_2) + H_{\text{oo}}(M_0, M_2) \quad (4)$$

Explicit forms of the terms in Eq. (4) have been given in [25,26,30]. The matrix of Hamiltonians in Eq. (1) is of the dimension  $252 \times 252$  and can be partitioned into four smaller matrices, i.e.  $E'\alpha'(62 \times 62)$ ,  $E'\beta'(62 \times 62)$ ,  $E''\alpha''(64 \times 64)$ , and  $E''\beta''(64 \times 64)$ . Details concerning the choice of the basis and calculation of the pertinent matrix elements have been published previously [25–27,31].

For  $\text{Fe}^{3+}$  ( $3d^5$  configuration) ion in the tetragonal symmetry crystal field (CF) the ground-state is the high-spin  ${}^6\text{A}_1$  state [32]. The magnetic interactions split  ${}^6\text{A}_1$  state into the effective spin states  $E'(\tilde{M}_s = \pm 1/2)$ ,  $E''(\tilde{M}_s = \pm 3/2)$ , and  $E''(\tilde{M}_s = \pm 5/2)$  [23]. According to the group theory [33], the process can be expressed as:

$$\text{A}_1 \otimes D^{(5/2)} \rightarrow \text{A}_1 \otimes (E' \oplus 2E'') \rightarrow E' \oplus E'' \oplus E'' \quad (5)$$

In order to describe this splitting  ${}^6\text{A}_1$ , the effective spin-Hamiltonian [23] should include the ZFS parameters  $a$ ,  $D$  and  $(a + 2F/3)$  [21] which can be analyzed by the effective spin Hamiltonian [23,34]

$$H_s = \frac{1}{3}DO_2^0 + \frac{1}{120}(a + \frac{2}{3}F)O_4^0 + \frac{1}{3}aO_4^4 \quad (6)$$

where the tetragonal axis  $z//4$ -fold axis,  $O_n^m$  ( $S_x, S_y, S_z$ ) are the Stevens operators [35,36]. Since the conventional ZFS parameters [21,23,34],  $b_2^0$ ,  $b_4^0$  and  $b_4^4$  are predominantly employed in EMR

studies for  $\text{Fe}^{3+}:\text{KMgF}_3$  [11], we use the conversion relations [15]:

$$b_2^0 = D \quad (7a)$$

$$2b_2^0 = a + \frac{2}{3}F \quad (7b)$$

$$b_4^4 = \frac{5}{2}a \quad (7c)$$

The microscopic spin Hamiltonian theory [21–23] enables to derive explicit expressions for the ZFS parameters in Eq. (6) in terms of the energy level separations obtained by the diagonalization of the *physical* Hamiltonian in Eq. (1). For tetragonal axial symmetry crystal field including the point groups  $\text{C}_{4v}$ ,  $\text{D}_4$ , and  $\text{D}_{2d}$ , the numbers of available ZFS transitions obtained from complete diagonalization method (CDM) are two, whereas those of the non-zero ZFS parameters are three. Since the number of available ZFS transitions is insufficient to determine all non-zero ZFS parameters, the approximation must be made. If the magnitude of the parameter  $\gamma = (1/2)\tan^{-1}\{\sqrt{5}a/[2(a + 2F/3) + 4D]\}$  is sufficiently small, we can obtain the approximated relations as follows [15,37]:

$$D \approx \frac{1}{28}(5\Delta_2 - \Delta_1) \quad (8a)$$

$$a + \frac{2}{3}F \approx \frac{1}{7}(\Delta_2 - 3\Delta_1) \quad (8b)$$

where the energy level separations  $\Delta_1$  and  $\Delta_2$  can be expressed as:

$$\Delta_1 = E_2 \left[ \left\langle E'' \left( \tilde{M}_s = \pm \frac{3}{2} \right) \right\rangle \right] - E_3 \left[ \left\langle E' \left( \tilde{M}_s = \pm \frac{1}{2} \right) \right\rangle \right] \quad (9a)$$

$$\Delta_2 = E_1 \left[ \left\langle E'' \left( \tilde{M}_s = \pm \frac{5}{2} \right) \right\rangle \right] - E_3 \left[ \left\langle E' \left( \tilde{M}_s = \pm \frac{1}{2} \right) \right\rangle \right] \quad (9b)$$

The energy level separations  $\Delta_1$  and  $\Delta_2$  are obtained by the diagonalization of the energy matrices within the full  $3d^5$  configuration. The experimental data [11] yield a very small  $\tan 2\gamma$  ( $\cong -0.017$ ) for the tetragonal center  $\text{Fe}^{3+}$  ions in  $\text{KMgF}_3$  crystals. Thus, Eq. (8) provides a good approximation for the tetragonal center  $\text{Fe}^{3+}$  ions in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals.

## 3. The tetragonal charge-compensation $\text{FeF}_5\text{O}$ defect model and CF parameters

In our calculations, we adopt the following parameters:  $B = 877.5 \text{ cm}^{-1}$ ,  $C = 3146.5 \text{ cm}^{-1}$ , and  $\xi_{\text{d}} = 371 \text{ cm}^{-1}$  [38] for  $\text{Fe}^{3+}$  in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals. It is found [30,39] for  $d^N$  configurations that the SS, SOO, and OO parameters:  $M_k(\text{SS}) = M_k(\text{SOO}) = M_k(\text{OO}) = M_k$  with  $k = 0$  and 2. Thus we adopt  $M_0 = 0.2917 \text{ cm}^{-1}$  and  $M_2 = 0.0229 \text{ cm}^{-1}$  [40] for  $\text{Fe}^{3+}$ . For fixed parameters  $B$ ,  $C$ ,  $\xi_{\text{d}}$ ,  $M_0$  and  $M_2$ , the ZFS parameters  $D$  and  $(a + 2F/3)$  as well as the energy level separations  $\Delta_1$  and  $\Delta_2$  of the ground state become only the functions of the CF parameters  $B_{20}$ ,  $B_{40}$  and  $B_{44}$ . This enables us to study the local structure distortion around  $\text{Fe}^{3+}$  defect centers for  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals.

The Newman superposition model [19,20] has proved to be a powerful tool in probing the local structure of TM ion in a variety of single crystals. In particular this method has been successfully applied to gain very detailed information on the lattice site and crystalline environment of  $\text{Fe}^{3+}$  ions in crystals [41,42]. Assuming the displacement of five ligand  $\text{F}^-$  toward the central metal ion  $\text{Fe}^{3+}$  is  $\Delta R_1(\text{F}^-)$  (see Fig. 1), the superposition model [19] yields the crystal field parameters  $B_{\text{kq}}$  due to the near-neighbor five fluorine

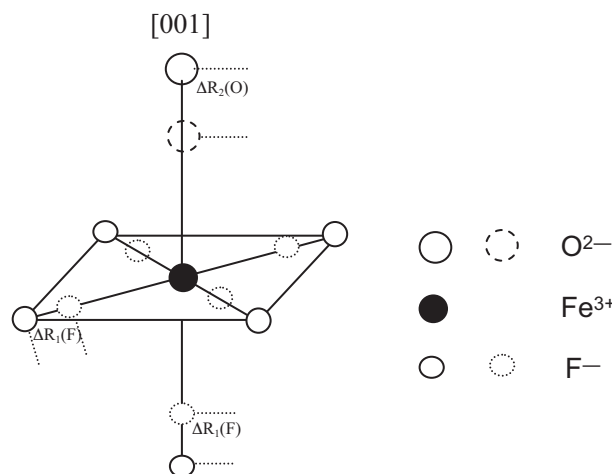


Fig. 1. Local lattice structure of the tetragonal  $\text{FeF}_5\text{O}$  cluster of  $\text{Fe}^{3+}$  center in  $\text{KMgF}_3$  crystals.

as:

$$B_{20} = -2\bar{A}_2(\text{F}^-) \left( \frac{R_0}{R_0 + \Delta R_1(\text{F})} \right)^{t_2} \quad (10a)$$

$$B_{40} = 20\bar{A}_4(\text{F}^-) \left( \frac{R_0}{R_0 + \Delta R_1(\text{F})} \right)^{t_4} \quad (10b)$$

$$B_{44} = 2\sqrt{70}\bar{A}_4(\text{F}^-) \left( \frac{R_0}{R_0 + \Delta R_1(\text{F})} \right)^{t_4}, \quad (10c)$$

whereas assuming the displacement of impurity  $\text{O}^{2-}$  toward the central metal ion  $\text{Fe}^{3+}$  is  $\Delta R_2(\text{O})$ , the superposition model yields the crystal field parameters  $B_{kq}$  due to the impurity  $\text{O}^{2-}$  as:

$$B_{20} = 2\bar{A}_2(\text{O}^{2-}) \left( \frac{R_0}{R_0 + \Delta R_2(\text{O})} \right)^{t_2}, \quad (11a)$$

$$B_{40} = 8\bar{A}_4(\text{O}^{2-}) \left( \frac{R_0}{R_0 + \Delta R_2(\text{O})} \right)^{t_4}, \quad (11b)$$

$$B_{44} = 0. \quad (11c)$$

In Eqs. (10) and (11),  $\bar{A}_k$  are the intrinsic parameters [19], and  $\bar{A}_k(\text{F}^-)$  ( $L = 2, 4$ ) are not equal to  $\bar{A}_k(\text{O}^{2-})$ .  $\bar{A}_4$  can be found from the relation for the cubic CF parameter  $Dq$  of ligands:  $\bar{A}_4 \approx 3Dq/4$  [43,44]. Using the experimental values:  $Dq(\text{Fe}^{3+} - 6\text{F}^-) = 1348 \text{ cm}^{-1}$  [38] for  $\text{Fe}^{3+}:\text{KMgF}_3$  yields  $\bar{A}_4(\text{F}^-) = 1011 \text{ cm}^{-1}$ , whereas  $Dq(\text{Fe}^{3+} - 6\text{O}^{2-}) = 1500 \text{ cm}^{-1}$  for  $\text{Fe}^{3+}$  ion in  $\text{Fe}^{3+}:\text{Al}_2\text{O}_3$  crystals [45] yields  $\bar{A}_4(\text{O}^{2-}) = 1125 \text{ cm}^{-1}$ . The ratio  $\bar{A}_2/\bar{A}_4$  tends to be a constant value for the iron-group ions [43,46,47]. It is taken as 10.8 in our calculations. The  $R_0 = 0.1987 \text{ nm}$ , i.e. the Fe–F distance in the perfect cubic site for  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals [11], is taken as the reference distance. We take the power-law exponents as  $t_2 = 3$ , and  $t_4 = 6$  [19,20] for ionic crystals  $\text{Fe}^{3+}:\text{KMgF}_3$ .

#### 4. Results and discussions

The relations (10) and (11) enable to investigate the variation of the CF parameters  $B_{kq}$  and, via Eq. (8), also of the ZFS parameters  $D$  and  $(a + 2F/3)$  as well as the energy level separations  $\Delta_1$  and  $\Delta_2$  as the functions of the crystal structural parameters  $R_1 (= R_0 + \Delta R_1(\text{F}))$  and  $R_2 (= R_0 + \Delta R_2(\text{O}))$ . To obtain the parameters  $D$  and  $(a + 2F/3)$  as well as  $\Delta_1$  and  $\Delta_2$ , we must diagonalize the Hamiltonian (1) for a given set of values of  $R_1$  and  $R_2$ . By simulating the ZFS parameters  $D$

Table 1

The energy level separations  $\Delta_1$ ,  $\Delta_2$  and the ZFS parameters  $D$ ,  $(a + 2F/3)$  for the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals as a function of  $R_1$  and  $R_2$ ;  $\Delta_1$ ,  $\Delta_2$ ,  $D$ , and  $(a + 2F/3)$  are in  $[10^{-4} \text{ cm}^{-1}]$ .

$R_1$ (nm)	$R_2$ (nm)	$\Delta_1$	$\Delta_2$	$D$	$(a + 2F/3)$
0.19796	0.18795	–7695	–22,012	–3656	153
	0.18805	–7608	–21,758	–3614	153
	0.18815	–7522	–21,505	–3572	152
	0.18825	–7437	–21,255	–3530	151
	0.18835	–7352	–21,006	–3489	150
<b>0.19806</b>	0.18795	–7690	–22,008	–3655	152
	0.18805	–7603	–21,755	–3613	151
	<b>0.18815</b>	<b>–7518</b>	<b>–21,506</b>	<b>–3572</b>	<b>150</b>
	0.18825	–7432	–21,254	–3530	149
	0.18835	–7348	–21,007	–3489	148
0.19816	0.18795	–7684	–22,003	–3655	150
	0.18805	–7598	–21,751	–3613	149
	0.18815	–7512	–21,501	–3571	148
	0.18825	–7428	–21,253	–3530	147
	0.18835	–7344	–21,007	–3489	146

Notes: the bold values  $R_1 = 0.19806 \text{ nm}$  and  $R_2 = 0.18815 \text{ nm}$  express the best fitted values of the crystal structural parameters whereas the bold values  $–7518$ ,  $–21506$ ,  $–3572$ , and  $–150$  [in  $10^{-4} \text{ cm}^{-1}$ ] are the corresponding values for the parameters  $D_1$ ,  $D_2$ ,  $D$ , and  $(a + 2F/3)$ , respectively.

and  $(a + 2F/3)$  as well as the energy level separations  $\Delta_1$  and  $\Delta_2$  simultaneously, we can obtain the parameters  $R_1$  and  $R_2$ . The theoretically calculated values of  $D$ ,  $(a + 2F/3)$ , and  $\Delta_1$ ,  $\Delta_2$  for a given set of values of the  $R_1$  and  $R_2$  are listed in Table 1. The results show that the best agreement for  $D$ ,  $(a + 2F/3)$ ,  $\Delta_1$ , and  $\Delta_2$  can be achieved for the crystal structural parameters  $R_1 = 0.19806 \text{ nm}$  and  $R_2 = 0.18815 \text{ nm}$  (see the bold values of Table 1). Using  $R_1 = R_0 + \Delta R_1(\text{F})$  and  $R_2 = R_0 + \Delta R_2(\text{O})$  with  $R_0 = 0.1987 \text{ nm}$ , we obtain the lattice distortion parameters  $\Delta R_1(\text{F}) = -6.40 \times 10^{-4} \text{ nm}$  and  $\Delta R_2(\text{O}) = -10.55 \times 10^{-3} \text{ nm}$ . The negative sign of  $\Delta R_1(\text{F})$  and  $\Delta R_2(\text{O})$  indicates a compression of the local structure of the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$ .

In order to explore the microscopic origin of the ZFS parameters  $D$  and  $(a + 2F/3)$ , we investigate four mechanisms (see Table 2). The results indicate that if the lattice distortions are not considered, a remarkably small  $D$ ,  $(a + 2F/3)$ ,  $\Delta_1$ , and  $\Delta_2$  are obtained (see Table 2 row a):  $D_{\text{cal}}/D_{\text{exp}} = 0.18$ ,  $(a + 2F/3)_{\text{cal}}/(a + 2F/3)_{\text{exp}} = 0.56$ ,  $\Delta_1_{\text{cal}}/\Delta_1_{\text{exp}} = 0.20$ , and  $\Delta_2_{\text{cal}}/\Delta_2_{\text{exp}} = 0.20$ . This shows that the lattice distortion must occur and play a significant role in contributing to these parameters. Due to the difference in mass, charge, and ionic radius between  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$ , the mutual interactions between the  $\text{Fe}^{3+}$  ion and five  $\text{F}^-$  ions or  $\text{O}^{2-}$  ion on the  $[001]$ -axis in doped crystals must differ from those between  $\text{Mg}^{2+}$  ion and six  $\text{F}^-$  ions in host crystals. Moreover, because the  $\text{Fe}^{3+}$  radius ( $0.064 \text{ nm}$ ) ion is smaller than that of the host  $\text{Mg}^{2+}$  ( $0.066 \text{ nm}$ ) ion, whereas the  $\text{Fe}^{3+}$  charge is larger than that of  $\text{Mg}^{2+}$ , the Coulomb interaction between  $\text{Fe}^{3+}$  ion and  $\text{F}^-$  ion in doped crystals is stronger than that between

Table 2

The calculated CF parameters, the energy level separations  $\Delta_1$ ,  $\Delta_2$  and the ZFS parameters  $D$ ,  $(a + 2F/3)$  arising from four mechanisms for the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals;  $\mu$  and  $\delta$  are in  $[\text{cm}^{-1}]$ , whereas  $\Delta_1$ ,  $\Delta_2$ ,  $D$ , and  $(a + 2F/3)$  are in  $[10^{-4} \text{ cm}^{-1}]$ .

	$\mu$	$\delta$	$\Delta_1$	$\Delta_2$	$D$	$(a + 2F/3)$
a	–1624.2	838.2	–1511	–3948	–651	83.6
b	–4923.7	1860.3	–7486	–21,486	–3569	139.0
c	–1466.2	785.1	–1360	–3457	–569	89.2
d	–4765.7	1807.3	–7518	–21,506	–3572	150
Expt. [11]			–7518	–21,508	–3572 ± 60	150 ± 10

a  $\text{O}^{2-}$  replacement:  $\Delta R_1(\text{F}) = 0$  and  $\Delta R_2(\text{O}) = 0$ .

b  $\text{O}^{2-}$  displacement:  $\Delta R_1(\text{F}) = 0$  and  $\Delta R_2(\text{O}) = -10.55 \times 10^{-3} \text{ nm}$ .

c  $\text{F}^-$  displacement:  $\Delta R_1(\text{F}) = -6.40 \times 10^{-4} \text{ nm}$  and  $\Delta R_2(\text{O}) = 0$ .

d Total:  $\Delta R_1(\text{F}) = -6.40 \times 10^{-4} \text{ nm}$  and  $\Delta R_2(\text{O}) = -10.55 \times 10^{-3} \text{ nm}$ .

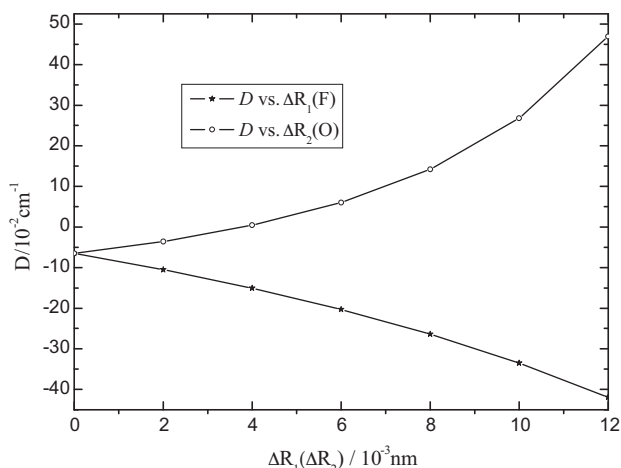


Fig. 2. Variation of the rank-2 ZFS parameter  $D$  with  $\Delta R_1(F)/\Delta R_2(O)$  for  $B = 877.5$ ,  $C = 3146.5$ ,  $\xi_a = 371$ ,  $M_0 = 0.2917$ ,  $M_2 = 0.0229$  (all in units  $\text{cm}^{-1}$ ).

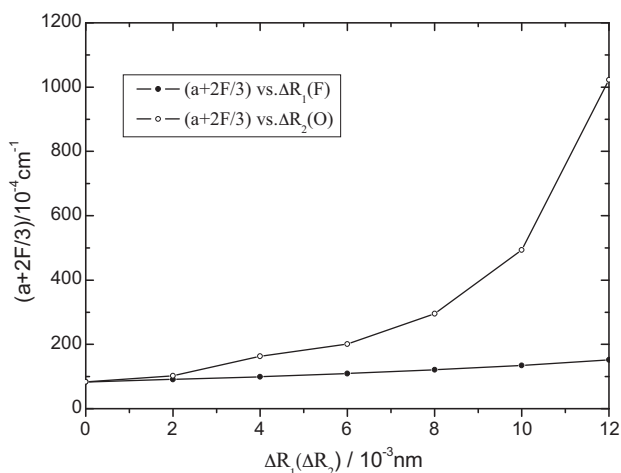


Fig. 3. Variation of the rank-4 ZFS parameter  $(a + 2F/3)$  with  $\Delta R_1(F)/\Delta R_2(O)$ , parameter values used are the same as in Fig. 2.

$\text{Mg}^{2+}$  and  $\text{F}^-$  ion in host crystals. Hence, it is reasonable to assume that the five  $\text{F}^-$  move toward the central  $\text{Fe}^{3+}$  ion in such an ionic crystal. Moreover, because the effective charge of  $\text{O}^{2-}$  on the  $[001]$ -axis is larger than that of the nearest five  $\text{F}^-$ , the Coulomb interaction between  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  ions is stronger than that between  $\text{Fe}^{3+}$  and  $\text{F}^-$  ions. Thus the re  $|\Delta R_1(F)| < |\Delta R_2(O)|$  seems acceptable.

Additionally, the ZFS parameters  $D$  and  $(a + 2F/3)$  with the local structure distortion parameters  $\Delta R_1(F)$  and  $\Delta R_2(O)$  for selected the range of  $\Delta R_1(F)$  and  $\Delta R_2(O)$  from 0 to 0.012 nm is plotted in Figs. 2 and 3. Fig. 2 indicates that  $D$  is very sensitive to changes in  $\Delta R_1(F)$  and  $\Delta R_2(O)$ . The contribution to  $D$  arising from the change  $\Delta R_1(F)$  of the  $\text{Fe}^{3+}\text{--F}^-$  distance is negative, whereas that arising from the change  $\Delta R_2(O)$  of the  $\text{Fe}^{3+}\text{--O}^{2-}$  distance for  $\Delta R_2(O) > 0.004$  nm is positive. Fig. 3 indicates  $(a + 2F/3)$  is very sensitive to the distortion parameter  $\Delta R_2(O)$ , whereas it is insensitive to  $\Delta R_1(F)$ .

## 5. Conclusions

We have made an investigation of the ZFS parameters and local lattice distortions for  $\text{Fe}^{3+}$  ions at the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals using the complete diagonalization method and considering the SS, SOO, and OO magnetic interactions in addition to the SO magnetic interaction. It was shown that the theoretical results of the ZFS parameters  $D$ ,  $(a + 2F/3)$  and the energy level separations of the ground states are in excellent agreement with the experimental ones when the five  $\text{F}^-$  ions move toward  $\text{Fe}^{3+}$

by  $|\Delta R_1(F)| = 6.4 \times 10^{-4}$  nm and the  $\text{O}^{2-}$  ion toward  $\text{Fe}^{3+}$  by  $|\Delta R_2(O)| = 10.55 \times 10^{-3}$  nm. In fact, due to the difference in mass, charge, and ionic radius between  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$ , the mutual interactions between the  $\text{Fe}^{3+}$  ion and five  $\text{F}^-$  ions or  $\text{O}^{2-}$  ion on the  $[001]$ -axis in doped crystals must differ from those between  $\text{Mg}^{2+}$  ion and six  $\text{F}^-$  ions in host crystals. Hence, the  $\text{O}^{2-}$  displacement  $|\Delta R_2(O)| = 10.55 \times 10^{-3}$  nm and  $\text{F}^-$  displacement  $|\Delta R_1(F)| = 6.4 \times 10^{-4}$  nm predicted based on the investigations of the ZFS of the ground states for  $\text{Fe}^{3+}$  ions at the tetragonal  $\text{FeF}_5\text{O}$  cluster center in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals are acceptable. This show that the local structure distortions play an important role in explaining the spectroscopic properties of  $\text{Fe}^{3+}$  in  $\text{Fe}^{3+}:\text{KMgF}_3$  crystals.

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## References

- [1] R. Hua, Z. Jia, D. Xie, C. Shi, Mater. Res. Bull. 37 (2001) 1189–1195.
- [2] F. Agnoli, W.L. Zhou, C.J. O'Connor, Adv. Mater. 13 (2001) 1697–1699.
- [3] Y. Tan, C. Shi, J. Solid State Chem. 150 (2000) 178–182.
- [4] A. Meijerink, J. Lumin. 55 (1993) 125–138.
- [5] Y. Valls, J.Y. Buzaré, M. Rousseau, J. Phys.: Condens. Matter 2 (1990) 3997–4003.
- [6] N.S. Altshuler, A.L. Larionov, Opt. Spectrosc. 66 (1989) 61–64.
- [7] O. Pilla, P.T.C. Freire, V. Lemos, Phys. Rev. B 52 (1995) 177–180.
- [8] H. Takeuchi, M. Arakawa, H. Ebisu, J. Phys. Soc. Jpn. 56 (1987) 3677–3682.
- [9] J.J. Krebs, R.K. Jeck, Phys. Rev. B 5 (1972) 3499–3505.
- [10] D.C. Stjern, R.C. DuVarney, Phys. Rev. B 10 (1974) 1044–1051.
- [11] H.S. Murrieta, J.O. Rubio, G.S. Aguilar, Phys. Rev. B 19 (1979) 5516–5524.
- [12] M. Binois, A. Leble, J.J. Rousseau, J.C. Fayet, J. Phys. Colloque C9 34 (1973) 285–288.
- [13] C. Rudowicz, P. Gnutek, Physica B 404 (2009) 3582–3593.
- [14] Z.Y. Yang, Y. Hao, C. Rudowicz, Y.Y. Yeung, J. Phys.: Condens. Matter 16 (2004) 3481–3494.
- [15] P. Gnutek, Z.Y. Yang, C. Rudowicz, J. Phys.: Condens. Matter 21 (2009) 455402–455413.
- [16] X.M. Tan, X.Y. Kuang, K.W. Zhou, Solid State Commun. 136 (2005) 359–399.
- [17] L. Qi, X.Y. Kuang, R.P. Chai, M.L. Duan, C.X. Zhang, Chin. Phys. B 18 (2009) 1586–1593.
- [18] Z.Y. Yang, Spectrochim. Acta Part A 75 (2010) 277–280.
- [19] D.J. Newman, B. Ng, Rep. Prog. Phys. 52 (1989) 699–763.
- [20] D.J. Newman, W. Urban, Adv. Phys. 24 (1975) 793–844.
- [21] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970, Dover, New York, 1986, pp. 365–466.
- [22] C. Rudowicz, S.K. Misra, Appl. Spectrosc. Rev. 36 (2001) 11–63.
- [23] C. Rudowicz, Magn. Reson. Rev. 13 (1987) 1–89;
- [24] C. Rudowicz, Magn. Reson. Rev. 13 (1988) 335 (Erratum).
- [25] Z.Y. Yang, C. Rudowicz, J. Qin, Physica B 318 (2002) 188–197.
- [26] Y. Hao, Z.Y. Yang, J. Magn. Magn. Mater. 299 (2006) 445–458.
- [27] C. Rudowicz, Z.Y. Yang, Y.Y. Yeung, J. Qin, J. Phys. Chem. Solids 64 (2003) 1419–1428.
- [28] Y.Y. Yeung, C. Rudowicz, Comput. Chem. 16 (1992) 207–216.
- [29] Z.Y. Yang, Q. Wei, Physica B 370 (2005) 137–145.
- [30] J.S. Griffith, Theory of Transition Metal Ions, Cambridge University Press, London, 1961.
- [31] B.G. Wybourne, Spectroscopic Properties of Rare Earths, John Wiley & Sons, Inc., New York, 1965, pp. 78–82.
- [32] Y.Y. Yeung, C. Rudowicz, J. Comput. Phys. 109 (1993) 150–152.
- [33] H.L. Schäfer, G. Gliemann, Basic Principles of Ligand Field Theory, Wiley-Interscience, London, 1969.
- [34] B.S. Tsukerblat, Group Theory in Chemistry and Spectroscopy, Academic Press, Harcourt Brace & Company Publishers, London, 1994, pp. 245–298.
- [35] R. Bramley, S.J. Strach, Chem. Rev. 83 (1983) 49–82.
- [36] C. Rudowicz, J. Phys. C 18 (1985) 1415–1430;
- [37] C. Rudowicz, J. Phys. C 18 (1985) 3837 (Erratum).
- [38] C. Rudowicz, J. Phys. C: Solid State Phys. 20 (1987) 6033–6037.
- [39] Z.Y. Yang, Physica B 405 (2010) 4740–4745.
- [40] W.L. Yu, C. Rudowicz, Phys. Rev. B 45 (1992) 9736–9748.
- [41] Z.B. Goldschmidt, Z. Vardi, Phys. Rev. A 31 (1985) 3039–3058.
- [42] S. Fraga, J. Karwowski, K.M.S. Saxena, Handbook of Atomic Data, Elsevier, Amsterdam, 1976, pp. 433–453.
- [43] S. Pandey, R. Kripal, J. Magn. Reson. 209 (2011) 220–226.
- [44] P. Gnutek, M. Ağıköç, C. Rudowicz, Opt. Mater. 32 (2010) 1161–1169.
- [45] W.L. Yu, J. Phys.: Condens. Matter 6 (1994) 5105–5112.
- [46] W.L. Yu, M.G. Zhao, Phys. Rev. B 37 (1988) 9254–9267.
- [47] J.J. Krebs, W.G. Maish, Phys. Rev. B 4 (1971) 757–769.
- [48] D.J. Newman, D.C. Pryce, W.A. Runciman, Am. Mineral. 63 (1978) 1278–1281.
- [49] Y.Y. Yeung, D.J. Newman, Phys. Rev. B 34 (1986) 2258–2265.