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# An investigation of the zero-field splitting of $Fe^{3+}$ ions at the tetragonal $FeF_5O$ site in $Fe^{3+}$:$KMgF_3$ crystals

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**Abstract.** The extremely large zero-field splitting of $Fe^{3+}$ ions at the tetragonal $FeF_5O$ site in $Fe^{3+}$:$KMgF_3$ crystals has been interpreted on the basis of a second- to sixth-order perturbation approach, in which the spin–orbit coupling is regarded as the perturbation to the crystal-field and electrostatic interactions. The replacement of $O^{2-}$ for $F^-$ and its induced lattice relaxation are shown to give rise to a strong tetragonal crystal field which in turn results in the large zero-field splitting. Of the various sources contributing to the zero-field splitting, the displacements of the $O^{2-}$ and $F^-$ ions are found to be important.

## 1. Introduction

$Fe^{3+}$ impurities replace divalent cations when they are doped into fluoroperovskite crystals $AMF_3$ (A represents an alkali metal and M represents an alkaline-earth metal ion). Defect sites will be formed owing to the charge compensation. Either trigonal A- or tetragonal M-vacancy sites have been observed in these crystals [1–6]. In the case of $KMgF_3$, a tetragonal defect site has been found by EPR experiments [5,6] in addition to a K-vacancy site [2]. This tetragonal site is characteristic of a very large rank-2 axial zero-field splitting (ZFS) ($|b_2^0| = 0.36$ cm$^{-1}$) [5,6], several times greater in magnitude than those ($|b_2^0| = 0.04$–$0.08$ cm$^{-1}$) for M-vacancy sites in $AMF_3$ crystals [3,4]; it has been assigned to an $FeF_5O$ configuration (figure 1) [5,6].

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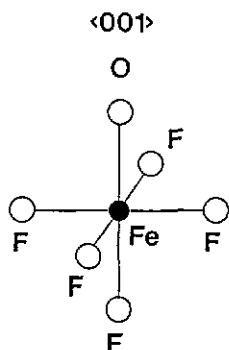

Figure 1. Coordination of $FeF_5O$ in $Fe^{3+}$:$KMgF_3$ crystals (without lattice relaxation).

Local lattice relaxation occurs when an $O^{2-}$ ion replaces an $F^-$ in the $\langle 001 \rangle$ axis to form an $FeF_5O$ cluster because of the difference in charge [5,6]. The replacement and the relaxation will give rise to a strong tetragonal crystal field (CF) which affects the ZFS through the spin–orbit (SO) coupling. Following this idea an investigation is made in the present work on the basis of a very convergent perturbation approach. The relaxation is found to play a major role in affecting the CF and ZFS.

## 2. Theory

The CF is expressed as ($z \parallel \langle 001 \rangle$)

$$\mathcal{H}_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}(C_4^{(4)} + C_{-4}^{(4)}) \tag{1}$$

where the $C_q^{(k)}$ are normalized spherical harmonics. It is convenient to define

$$Dq = \frac{1}{42}\left(B_{40} + \sqrt{\frac{14}{5}}B_{44}\right)$$

$$B'_{40} = B_{40} - \sqrt{\frac{14}{5}}B_{44}. \tag{2}$$

$B_{20}$ and $B'_{40}$ vanish identically in cubic symmetry and thus they as well as $Dq' \equiv Dq - Dq_c$ present a measurement of the net charge compensation contribution to the CF, where $Dq_c$ denotes the CF parameter of the cubic site.

The CF parameters are given in the superposition model as [7]

$$B_{kq} = (-1)^q S_k^{-1} \sum_L \bar{A}_k(R_L) C_{-q}^{(k)}(\Theta_L, \Phi_L) \tag{3}$$

where $S_2 = \frac{1}{2}$, $S_4 = \frac{1}{8}$. The summation is over all ligands. $\bar{A}_k$ ($k = 2, 4$) are called intrinsic parameters and they are expressed in the power law as [7]

$$\bar{A}_k(R_L) = \bar{A}_k(R_0)\left(\frac{R_0}{R_L}\right)^{t_k} \tag{4}$$

where $R_0$ is a reference distance. The following relations hold: $\bar{A}_2 \gg \bar{A}_4 > 0$ and $t_4 > t_2 > 0$, where $\bar{A}_k \equiv \bar{A}_k(R_0)$ [7]. In particular, the ratio $\bar{A}_2/\bar{A}_4$ tends to a constant of about 11 for iron-group ions [8–11]; it is taken to be 10.8 in our calculations. However, the $\bar{A}_k$ are dependent of the ligand. If $R_0$ is taken as the $Fe^{3+} - F^-$ distance in the perfect cubic site, $\bar{A}_4^F$ and $\bar{A}_4^0$ are obtained to be 1011 cm$^{-1}$ and 1125 cm$^{-1}$, respectively, from the relation $\bar{A}_4 = \frac{3}{4}Dq_c$ [12] with $Dq_c(Fe^{3+} - 6F^-) = 1348$ cm$^{-1}$ [13] found for $Fe^{3+}$:$KMgF_3$ and $Dq_c(Fe^{3+}-6O^{2-}) = 1500$ cm$^{-1}$ observed for $Fe^{3+}$:$Al_2O_3$ [14,15]. $t_2 = 3$ and $t_4 = 5$ are adopted in our calculations for the ionic bonds [7].

We now consider the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{CF} + \mathcal{H}_{SO} \tag{5}$$

where $\mathcal{H}_0$ denotes the electrostatic interaction, $\mathcal{H}_{CF}$ the CF interaction and $\mathcal{H}_{SO}$ the SO interaction. The spin–spin interaction is omitted owing to its weakness. Our calculations for the Hamiltonian matrix elements are carried out in the intermediate CF coupling scheme [16].

The symmetry-adapted basis function of a component $\gamma$ of an irreducible representation $\Gamma$ of the double group $C'_{4v}$ is expressed in terms of the product of the orbit part $|d^N\alpha L\Gamma_L\gamma_L\rangle$ and the spin part $|d^N\alpha S\Gamma_S\gamma_S\rangle$:

$$|d^N\alpha SL\Gamma\gamma\rangle = \sum_{\Gamma_L}\sum_{\Gamma_S} C(\Gamma_L\gamma_L\Gamma_S\gamma_S; \Gamma\gamma)|d^N\alpha L\Gamma_L\gamma_L\rangle|d^N\alpha S\Gamma_S\gamma_S\rangle \qquad (6)$$

where

$$|d^N\alpha L\Gamma_L\gamma_L\rangle = \sum_{M_L} C(LM_L; \Gamma_L\gamma_L)|d^N\alpha LM_L\rangle$$

$$|d^N\alpha S\Gamma_S\gamma_S\rangle = \sum_{M_S} C(SM_S; \Gamma_S\gamma_S)|d^N\alpha SM_S\rangle \qquad (7)$$

with $C$ denoting the coupling coefficients. The matrix elements of $\mathcal{H}_{\text{CF}}$ and $\mathcal{H}_{\text{SO}}$ are given by the following formulae:

$$\langle d^N\alpha SLM_SM_L|\mathcal{H}_{\text{CF}}|d^N\alpha'S'L'M'_SM'_L\rangle$$

$$= \delta(M_SM'_S)\delta(SS')\sum_{kq} B_{kq}\langle d\|C^{(k)}\|d\rangle(-1)^{L-M_L}$$

$$\times \begin{bmatrix} L & k & L' \\ -M_L & q & M'_L \end{bmatrix}\langle d^N\alpha SL\|V^{(k)}\|d^N\alpha'S'L'\rangle \qquad (8)$$

$$\langle d^N\alpha SLM_SM_L|\mathcal{H}_{\text{SO}}|d^N\alpha'S'L'M'_SM'_L\rangle$$

$$= \langle d\|l^{(1)}\|d\rangle\langle d^N\alpha SL\|V^{(11)}\|d^N\alpha'S'L'\rangle\zeta\sum_{q=-1}^{1}(-1)^{q+S+L-M_S-M_L}$$

$$\times \begin{bmatrix} S & 1 & S' \\ -M_S & -q & M'_S \end{bmatrix}\begin{bmatrix} L & 1 & L' \\ -M_L & q & M'_L \end{bmatrix}. \qquad (9)$$

In the expressions, $(\ldots)$ are $3j$ symbols and $\zeta$ the spin–orbit coupling constant. The reduced matrix elements $\langle d^N\alpha SL\|U^{(k)}\|d^N\alpha'S'L'\rangle$ and $\langle d^N\alpha SL\|V^{(11)}\|d^N\alpha'S'L'\rangle$ have been given in [17]. In the intermediate CF coupling scheme, $\mathcal{H}_0$ is diagonal, $\mathcal{H}_{\text{CF}}$ is block diagonal and $\mathcal{H}_{\text{SO}}$ couples the blocks. Thus this scheme is suitable for the iron-group $3d^N$ ions where $|\langle\mathcal{H}_{\text{SO}}\rangle| \ll |\langle\mathcal{H}_{\text{CF}}\rangle| \approx |\langle\mathcal{H}_0\rangle|$. There are two doubly degenerate irreducible representations $E'$ and $E''$ for $C'_{4v}$. The Hamiltonian matrices are both $64 \times 64$ dimensional in the case of $3d^5$. The matrix elements and the ZFS parameters are calculated by using a carefully checked FORTRAN program.

The spin-Hamiltonian is written as $(S = \tfrac{5}{2})$

$$\mathcal{H}_S = \tfrac{1}{3}b_2^0 O_2^0 + \tfrac{1}{60}(b_4^0 O_4^0 + b_4^4 O_4^4) \qquad (10)$$

where $O_k^q = O_k^q(S_x, S_y, S_z)$ are Stevens operators and $b_k^q$ the ZFS parameters. Considering the ZFS as a result of the combined interaction of CF and SO terms, the ZFS parameters are calculated by a high-order perturbation approach [13]. The SO term is regarded as a perturbation to the CF and the electrostatic interactions for it is one order of magnitude less. In this procedure, the SO term begins to affect the rank-2 ZFS terms $b_2^q$ at second order and the rank-4 terms $b_4^q$ at fourth order [13]. Our calculations are carried out to sixth order and by taking into account all states in the $3d^5$ configuration. The results show excellent convergence, as can be seen in the next section.

## 3. Results

The point symmetry reduces from $O_h$ to $C_{4v}$ when $O^{2-}$ replaces $F^-$ on the $\langle 001\rangle$ axis. Owing to the different CF interactions for the host and impurity ions, the replacement gives rise to a contribution to tetragonal CF components with $B_{20} = 2462$ cm$^{-1}$ and $B_{40} = 912$ cm$^{-1}$. Meanwhile, the cubic CF parameter $Dq$ changes from 1348 cm$^{-1}$ of the perfect cubic site [13] to 1370 cm$^{-1}$. By using these CF parameters as well as $B = 877.5$ and $C = 3146.5$ as the Racah parameters, $\alpha = 64.5$ as the Trees correction and $\zeta = 371$ as the SO constant [13], we obtain the following ZFS parameters: $b_2^0 = -0.0615$ cm$^{-1}$, $b_4^0 = 0.0032$ cm$^{-1}$ and $b_4^4 = 0.0125$ cm$^{-1}$, which are considerably less than the experimental findings [6]: $b_2^0 = -0.3572$ cm$^{-1}$, $b_4^0 = 0.0075$ cm$^{-1}$ and $b_4^4 = 0.0269$ cm$^{-1}$. This shows that a lattice relaxation must occur and play a significant role in contributing to the ZFS.

The sizes of the host $F^-$ and substituted $O^{2-}$ ions are quite similar. However, because of the difference between their charges, the impurity $O^{2-}$ itself and ions around it will move away from their original positions. Although the final equilibrium positions depend on the potential of the whole crystal, the EPR experimental results can provide good information concerning the lattice relaxation.

It is reasonable to assume that $O^{2-}$ and the central magnetic $Fe^{3+}$ ion move towards one another in such an ionic crystal where the Coulomb interaction serves as the main crystallized source [5, 6]. However, the displacement of $Fe^{3+}$, denoted by $\Delta(Fe^{3+})$, is found to have a very small contribution to the CF and thus to the ZFS properties, compared with $O^{2-}$. It is neglected in our first-approximation calculations.

If we denote the displacement of $O^{2-}$ as $\Delta(O^{2-})$, the ZFS parameters are calculated as functions of $\Delta(O^{2-})/R_0$ as plotted in figure 2, where $R_0$ represents the $Fe^{3+}$–$F^-$ distance in the perfect cubic site. As can be seen, systematic agreement with every experimental ZFS parameter does not appear at a specific value of $\Delta(O^{2-})/R_0$. Movements of the four planar $F^-$ ions have to be taken into account [6].

The inward displacement of the equivalent planar $F^-$ ions is denoted as $\Delta(F^-)$. In figure 2, $b_2^0$, $b_4^0$ and $b_4^4$ are shown as functions of $\Delta(O^{2-})/R_0$ with $\Delta(F^-)/R_0 = 0$, 0.01, 0.02 and 0.03. The experimental values [6] are plotted as horizontal lines, with the solid curves representing the mean values and the dashed lines covering the experimental errors. The figure shows that systematic agreement with the experimental ZFS parameters is reached at $\Delta(F^-)/R_0 \approx 0.02 \pm 0.002$ and $\Delta(O^{2-})/R_0 = 0.078 \pm 0.002$ with the assumption $\Delta(Fe^{3+}) = 0$.

The electron–nuclear double-resonance experimental superhyperfine results have indicated a slight displacement of the central iron ion toward $O^{2-}$ [5]. When this movement is taken into account in the range $\Delta(Fe^{3+}) = (0–0.03)R_0$, the values of $\Delta(O^{2-})$ are found to lie in the range $(0.065–0.078)R_0$, with $\Delta(F^-) = 0.02R_0$ fixed in the reproduction of the experimental ZFS data. A slight change in the value of $\Delta(O^{2-})$ appears with variation in $\Delta(Fe^{3+})$. $\Delta(Fe^{3+})$ is reasonably expected to be $(0.02 \pm 0.01)R_0$ [6], although its value cannot be determined effectively as we have done for $\Delta(O^{2-}) = (0.07 \pm 0.01)R_0$ and $\Delta(F^-) = (0.020 \pm 0.002)R_0$. The value of $R_0$ has been estimated to be 1.986 Å [18]. Thus our results can be expressed as $\Delta(O^{2-}) = 0.14 \pm 0.02$ Å, $\Delta(Fe^{3+}) = 0.04 \pm 0.02$ Å and $\Delta(F^-) = 0.040 \pm 0.004$ Å.

## 4. Discussion

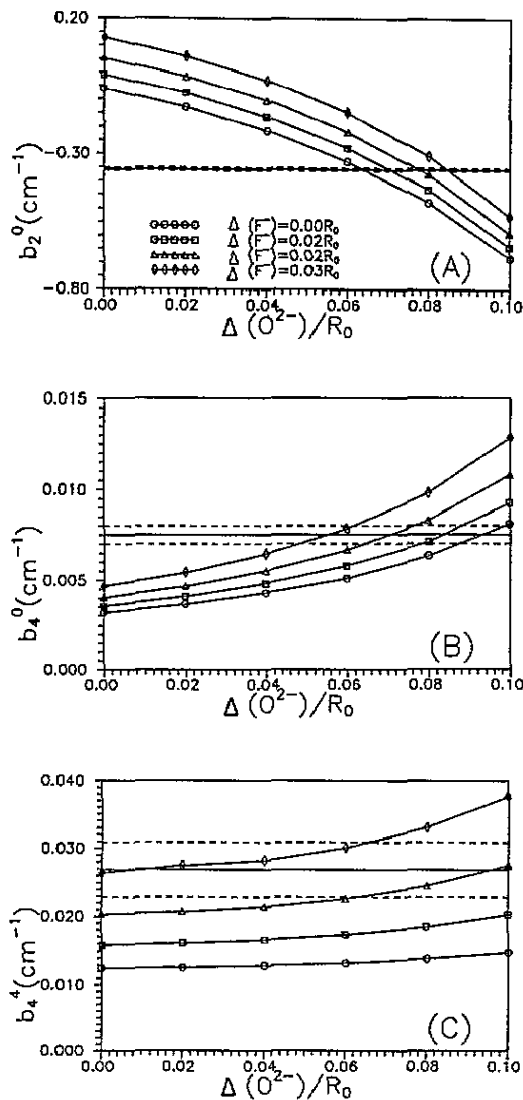In table 1 we show the second- to sixth-order contributions to the ZFS parameters for the following cases:

**Figure 2.** ZFS parameters (a) $b_2^0$, (b) $b_4^0$ and (c) $b_4^4$ of the FeF$_5$O site in Fe$^{3+}$:KMgF$_3$ crystals as functions of $\Delta(O^{2-})/R_0$. $\Delta(Fe^{3+})$ is taken to be zero in teh calculations of the theoretical values indicated by the centred symbols. The experimental results [6] are shown by the horizontal lines: ——, mean values; – – –, errors.

(i) without a relaxation of $(\Delta(O^{2-}) = \Delta(F^-) = \Delta(Fe^{3+}) = 0)$;

(ii) with a relaxation of $\Delta(O^{2-})/R_0 = 0.069$, $\Delta(F^-)/R_0 = 0.02$ and $\Delta(Fe^{3+})/R_0 = 0.02$.

The results show that relaxation must occur, because calculated values for (i) are significantly lower than the experimental data. Very good convergence can be seen in both cases, as should be so because of the weakness of the perturbation Hamiltonian SO term. One can also see that the rank-2 ZFS $b_2^0$ comes predominantly from the second and third orders while the rank-4 terms $b_4^0$ and $b_4^4$ from the fourth and fifth orders with higher orders negligible, as has been pointed out in our previous work [13].

**Table 1.** ZFS parameters resulting from various perturbation orders for the FeF$_5$O site in Fe$^{3+}$:KMgF$_3$ crystals.

| | $\Delta(O^{2-}) = 0$, $\Delta(Fe^{3+}) = 0$, $\Delta(F^-) = 0$ | | | $\Delta(O^{2-}) = 0.069R_0$, $\Delta(Fe^{3+}) = 0.02R_0$, $\Delta(F^-) = 0.02R_0$ | | |
|---|---|---|---|---|---|---|
| | $b_2^0$ (cm$^{-1}$) | $b_4^0$ (cm$^{-1}$) | $b_4^4$ (cm$^{-1}$) | $b_2^0$ (cm$^{-1}$) | $b_4^0$ (cm$^{-1}$) | $b_4^4$ (cm$^{-1}$) |
| *Second order* | −0.0518 | | | −0.3247 | | |
| Third order | −0.0100 | | | −0.0382 | | |
| Fourth order | +0.0004 | 0.0027 | 0.0103 | +0.0024 | 0.0069 | 0.0191 |
| Fifth order | −0.0001 | 0.0004 | 0.0021 | −0.0003 | 0.0011 | 0.0050 |
| Sixth order | +0.0000 | 0.0000 | 0.0001 | +0.0000 | 0.0001 | 0.0003 |
| Total | −0.0615 | 0.0031 | 0.0125 | −0.3608 | 0.0081 | 0.0244 |
| Experimental[a] | −0.3572 | 0.0075 | 0.0269 | −0.3572 | 0.0075 | 0.0269 |
| | ±0.0060 | ±0.0005 | ±0.0040 | ±0.0060 | ±0.0005 | ±0.0040 |

[a] from [6].

**Table 2.** CF and ZFS parameters resulting from various sources for the FeF$_5$O site in Fe$^{3+}$:KMgF$_3$ crystals, calculated for $\Delta(O^{2-})/R_0 = 0.069$, $\Delta(Fe^{3+})/R_0 = 0.02$ and $\Delta(F^-)/R_0 = 0.02$.

| | $B_{20}$ (cm$^{-1}$) | $B'_{40}$ (cm$^{-1}$) | $Dq$ (cm$^{-1}$) | $D$ (cm$^{-1}$) | $F$ (cm$^{-1}$) | $a$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| Perfect | 0 | 0 | 1348 | 0 | 0 | 0.0051 |
| O$^{2-}$ replacement | 2462 | 912 | 22 | −0.0615 | 0.0021 | −0.0003 |
| O$^{2-}$ displacement | 5814 | 3868 | 92 | −0.3289 | 0.0068 | 0.0004 |
| F$^-$ displacement | −2729 | −1719 | 102 | +0.1112 | −0.0027 | 0.0032 |
| Fe$^{3+}$ displacement | 157 | 71 | 1 | −0.0043 | 0.0001 | −0.0000 |
| Coherent | 668 | 612 | 15 | −0.0773 | 0.0034 | 0.0013 |
| Total | 6372 | 3744 | 1580 | −0.3608 | 0.0097 | 0.0097 |
| Experiment[a] | | | | −0.3572 | 0.0064 | 0.0108 |
| | | | | ±0.0060 | ±0.0040 | ±0.0016 |

[a] from [6].

To obtain more insight into the results, it is helpful to adopt the conventional notations for the ZFS parameters: $D = b_2^0$, $F = 3(b_4^0 - \frac{1}{5}b_4^4)$ and $a = \frac{2}{5}b_4^4$. The parameters $D$, $F$ and $a' \equiv a - a_c$ are zero in cubic symmetry and thus they represent the net charge compensation ZFS effect [19], where $a_c = 0.005\,12 \pm 0.000\,05$ cm$^{-1}$ is the ZFS for the cubic site [20]. The calculated values $D = -0.3608$ cm$^{-1}$, $F = 0.0097$ cm$^{-1}$ and $a' = 0.0047$ cm$^{-1}$ for case (ii) are in good agreement with the experimental results $D = -0.3572 \pm 0.0060$ cm$^{-1}$, $F = 0.0064 \pm 0.0040$ cm$^{-1}$ and $a' = 0.0057 \pm 0.0016$ cm$^{-1}$ [6]. These parameters are non-zero owing to the net charge compensation CF effect and they are large because of the strong tetragonal distortion having $B_{20} = 6372$ cm$^{-1}$, $B'_{40} = 3744$ cm$^{-1}$ and $Dq' = 232$ cm$^{-1}$ (table 2). It has been shown that $D$ arises mainly from $B'_{40}$, while $F$ arises mainly from $B_{20}$, through the combined interaction with the cubic part of CF and the SO interaction [13]. The increase of $a' = 0.0057$ cm$^{-1}$ in the value of $a$ results mostly from the increase of $Dq' = 232$ cm$^{-1}$ in the value $Dq$, whose contribution is calculated to be 0.0072 cm$^{-1}$. The tetragonal components, mainly $B_{20}$ [13], have a negative and non-negligible contribution of $a_t = -0.0025$ cm$^{-1}$. It is mentioned that the calculated $a_t/F$-value of −0.26 supports the theoretical prediction $a_t/F = -(0.2–0.5)$ for Mn$^{2+}$ and Fe$^{3+}$ ions in our previous work [13].

The CF potential is considered to be composed of the following contributions:

(a) the perfect lattice (i.e. without defects);
(b) the replacement of $O^{2-}$ for $F^-$;
(c) displacements of $O^{2-}$, $Fe^{3+}$ and $F^-$;
(d) additonally the coherent contribution of (a)–(c).

The ZFS is considered similarly. In table 2 we show these contributions separately, obtained for $\Delta(O^{2-})/R_0 = 0.069$, $\Delta(Fe^{3+})/R_0 = 0.02$ and $\Delta(F^-)/R_0 = 0.02$. As can be seen, the perfect lattice has no contributioin to $D$, $F$ and $a'$. The contribution of the $O^{2-}$ replacement to $D$ and $F$ is positive and the contribution to $a$ is small and negative. The displacement of $O^{2-}$ is the main source for the axial ZFS parameters $D$ and $F$, although it is negligible in affecting $a$. The contribution of $F^-$ displacement to $D$ and $F$ is negative but the contribution to $a$ is large. The displacement of $Fe^{3+}$ plays a negligible role in the ZFS. The coherent contributions arising from non-linear terms are important.

The results $\Delta(O^{2-})/R_0 = 0.07 \pm 0.01$, $\Delta(Fe^{3+})/R_0 = 0.02 \pm 0.01$ and $\Delta(F^-)/R_0 = 0.02 \pm 0.002$ obtained are compared with $\Delta(Fe^{3+})/R_0 = 0.01$–$0.02$ and $\Delta(F^-)/R_0 = 0.04$–$0.06$ obtained by Murrieta *et al* [6] from a superposition model analysis under the assumption of $\Delta(O^{2-}) = 0$. The difference between the results arises because of the difference between the theories used. Our results have indicated the importance of $\Delta(O^{2-})$ in the contribution to the ZFS.

## 5. Summary

The very large ZFS parameters observed for the FeF₅O defect site in $Fe^{3+}$:KMgF₃ have been interpreted in the framework of the CF theory. The replacement of $O^{2-}$ for $F^-$ and its induced lattice relaxation give rise to large tetragonal CF components and they cause a great increase in the cubic CF part. It is the resulting CF that makes the ZFS very large through the interaction with the SO coupling. The lattice relaxation is the main factor in this procedure. The experimental ZFS parameters can be reproduced well by assuming that $O^{2-}$ moves towards $Fe^{3+}$ by $(0.07 \pm 0.01)R_0$, $Fe^{3+}$ towards $O^{2-}$ by $(0.02 \pm 0.01)R_0$, and the planar $F^-$ ions towards the centre by $(0.02 \pm 0.002)R_0$.

## Acknowledgments

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