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AN INVESTIGATION FOR THE Cd^{2+}-VACANCIES IN $RbCdF_3$ and $CsCdF_3$ CRYSTALS DOPED WITH Fe^{3+} IMPURITIES*

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This paper presents high-order perturbation calculations for the zero-field splitting parameters D, F, and a of Fe^{3+}-V_{Cd} pairs in $RbCdF_3$ and $CsCdF_3$ crystals doped with Fe^{3+} impurities. In comparison with experimental data, the present results are better than those obtained in previous work by using the phenomenological superposition model of spin-Hamiltonian. Moreover, the crystal fields arising from the Cd^{2+}-vacancy and their induced crystal lattice distortion are analysed and calculated. It is found that the contribution from the Cd^{2+}-vacancies cannot be ignored. Meanwhile, we obtain that a ligand F^- along the [001]-axis moves towards the central Fe^{3+} ion by $\Delta = 0.0020$ nm in $RbCdF_3$ and 0.0028 nm in $CsCdF_3$. These results are quite different from $\Delta = 0.0104$ nm and $\Delta = 0.0112$ nm, respectively, obtained in previous work by using the superposition model of spin-Hamiltonian and ignoring the effect of the vacancy.

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I. INTRODUCTION

It is known that Fe^{3+} impurities substitute for Cd^{2+} cations in $RbCdF_3$ and $CsCdF_3$ crystals. Owing to the differences in charge, mass, and radius between Fe^{3+} and Cd^{2+} ions, a Cd site on [001]-axis will be vacant (V_{Cd}). Meanwhile, the local structure distorts and the local point symmetry around Fe^{3+} changes from O_h to C_{4v}[1]. This has been confirmed by electron paramagnetic resonance (EPR) experiments[1]. Information about the local structure distortion can be obtained from the EPR data of zero-field splitting (ZFS) parameters D, F, and a. Recently, Takeuchi *et al.*[1] have analysed the ZFS parameters by using the phenomenological superposition model[2,3] and they have obtained that a F^- ion on a [001]-axis of the crystals moves towards the central metal ion by $\Delta = 0.0104$ nm for $RbCdF_3$ and $\Delta = 0.0112$ nm for $CsCdF_3$. In their calculations the effect of the Cd^{2+} vacancy has been ignored. The present work carries out high-order perturbation calculations, taking into account both the effect of lattice distortion and of Cd^{2+} -vacancy. We obtain that $\Delta(RbCdF_3)$=0.0020 nm, and $\Delta(CsCdF_3)$=0.0028 nm. The results indicate that the effect of the Cd^{2+}-vacancies can not be neglected. The approach used in the present work for handling EPR data of cation-vacancy pairs is applicable to other situations as well.

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II. HIGH-ORDER PERTURBATION CALCULATIONS FOR THE ZERO-FIELD SPLITTING PARAMETERS

The spin-Hamiltonian for a ^6S-state ion in crystal field with tetrahedral symmetry can be written as[3]

$$H_s = (\boldsymbol{H}\cdot\boldsymbol{g})S + \frac{1}{3}b_2^0O_2^0 + \frac{1}{60}[b_4^0O_4^0 + b_4^4O_4^4], \tag{1}$$

w here $O_k^q = O_k^q(S_x, S_y, S_z)$. The ZFS parameters b_k^q are related to the conventional ones frequently used in literature by the following expressions[3]:

$$D = b_2^0,\ a = \frac{2}{5}b_4^4,\ F = 3(b_4^0 - \frac{1}{5}b_4^4). \tag{2}$$

Let us consider the Hamiltonian

$$H = H_0 + H_{cf} + H_{so}, \tag{3}$$

where H_0 denotes the electrostatic interaction, H_{cf} the crystal field, and H_{so} the spin-orbit coupling. The crystal field with tetragonal symmetry is given as

$$H_{cf} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}\left[C_4^{(4)} + C_{-4}^{(4)}\right], \tag{4}$$

where B_{kq} are crystal field parameters and $C_q^{(k)} = \left[\frac{4\pi}{2k+1}\right]^{1/2} Y_{kq}$ with Y_{kq} denoting spherical harmonics. It is convenient to define $D_q = \frac{1}{42}\left[B_{40} + \sqrt{\frac{14}{5}}B_{44}\right]$ and $B'_{40} = B_{40} - \sqrt{\frac{14}{5}}B_{44}$. The parameter B'_{40} vanishes identically in crystals with cubic symmetries as B_{20} does. Thus B_{20} and B'_{40} denote the tetragonal crystal field components and D_q the cubic one.

Under the combined interaction of H_{so} and H_{cf}, the ground state ^6S of a $3d^5$ ion splits into three Kramers levels in a crystal of tetragonal symmetry. The splitting is measured by three ZFS parameters D, F, and a. In calculation of D, the previous works have regarded part or whole of H_{cf}, together with H_{so}, as perturbation Hamiltonian. The consequent convergency is not very good as one would expect[4]. Calculation for the fourth-rank ZFS parameters a and F is more complicated and involves tedious labour since the spin-doublets and fifth order perturbation have to be included[4,5]. The present work treats H_{so} as the perturbation to H_0 and H_{cf} in the calculation of D, F, and a. The resulting perturbation convergency is very good since for $3d^5$ ions, $|\langle H_{so}\rangle|$ is usually two orders of magnitude smaller than the energy seperations between the ground and the excited state owing to the fact that $|\langle H_{so}\rangle| \ll |\langle H_{cf}\rangle| \leq |\langle H_0\rangle|$[4].

Our calculations are carried out in the intermediate crystal field coupling scheme[4]: The symmetry-adapted basis function of a component γ of an irreducible representation Γ 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 $|\, d^N\alpha S\Gamma_s\gamma_s\rangle$,

$$|\, d^N\alpha SL\Gamma\gamma\rangle = \sum_{\Gamma_L}\sum_{\Gamma_S} C(\Gamma_L\gamma_L\Gamma_s\gamma_s;\Gamma\gamma)\,|\, d^N\alpha L\Gamma_L\gamma_L\rangle\,|\, d^N\alpha S\Gamma_s\gamma_s\rangle, \tag{5}$$

where

$$\begin{aligned} |\, d^N\alpha L\Gamma_L\gamma_L\rangle &= \sum_{M_L} C(LM_L;\Gamma_L\gamma_L)\,|\, d^N\alpha LM_L\rangle, \\ |\, d^N\alpha S\Gamma_S\gamma_S\rangle &= \sum_{M_S} C(SM_S;\Gamma_S\gamma_S)\,|\, d^N\alpha SM_S\rangle, \end{aligned} \tag{6}$$

with C denoting the coupling coefficients. The matrix elements of $H_{\rm cf}$ and $H_{\rm so}$ are given by the following formulas:

$$\langle d^N\alpha SLM_SM_L \mid H_{\rm cf} \mid d^N\alpha'S'L'M_S'M_L'\rangle = \delta(M_SM_S')\delta(SS')\sum_{kq} B_{kq}\langle d \parallel C^{(k)} \parallel d\rangle$$

$$\times(-1)^{L-M_L}\begin{bmatrix} L & k & L' \\ -M_L & q & M_L' \end{bmatrix}\langle d^N\alpha SL \parallel U^{(k)} \parallel d^N\alpha'S'L'\rangle, \tag{7}$$

$$\begin{aligned} &\langle d^N\alpha SLM_SM_L \mid H_{\rm so} \mid d^N\alpha'S'L'M_S'M_L'\rangle \\ &= \langle d \parallel l^{(1)} \parallel d\rangle\langle d^N\alpha SL \parallel V^{(11)} \parallel d^N\alpha'S'L'\rangle\zeta \\ &\times\sum_{q=-1}^{1}(-1)^{q+S+L-M_S-M_L}\begin{pmatrix} S & 1 & S' \\ -M_S & -q & M_S' \end{pmatrix}\begin{pmatrix} L & 1 & L' \\ -M_L & q & M_L' \end{pmatrix}. \end{aligned} \tag{8}$$

In the expressions, $(\cdots)$ are $3j$ symbols and ζ the spin-orbit coupling constant. The reduced matrix elements $\langle d^N\alpha SL \parallel U^{(k)} \parallel d^N\alpha'S'L'\rangle$ and $\langle d^N\alpha SL \parallel V^{(11)} \parallel d^N\alpha'S'L'\rangle$ are given in Ref. [6].

In the intermediate crystal field coupling scheme, H_0 is diagonal while $H_{\rm cf}$ is block-diagonal[4]. Thus this scheme is very suitable for the iron-group $3d^n$ ions since it can result in reasonable energy splitting scheme in the situations where $|\langle H_{so}\rangle| \ll |\langle H_{cf}\rangle| \leq |\langle H_0\rangle|$. Also, the calculation can be made easier and the obtained matices are simple in form. In the expressions (7) and (8), the Racah irreducible tensor operator technique has been applied, reducing calculations significantly and making it convenient to apply computers. We carry out the calculations with a FORTRAN program to fifth-order perturbation and by taking into account all the 252 states in the $3d^5$ configuration. The input data include the Racah parameters B and C, the Trees correction constant α, the crystal field parameters B_{20}, B_{40}', and D_q, as well as the spin-orbit coupling coefficient ζ, and the output results are D, F, and a. The value of the ZFS parameter a in the case of cubic symmetry, denoted by a_c, can be obtained by assuming $B_{20} = B_{40}' = 0$.

It follows from optical absorption experiments[7] that $B = 877.6\,\mathrm{cm}^{-1}$, $C = 3146.5\,\mathrm{cm}^{-1}$, and $\alpha = 64.5\,\mathrm{cm}^{-1}$ for Fe^{3+} ions in $Li_3Na_3Fe_2F_{12}$ crystals. Since the values of these parameters as well as that of ζ depend mainly on the ligand, we assume that the Fe^{3+} ions in $RbCdF_3$ and $CsCdF_3$ crystals have identical values of B, C, α, and ζ to those in $Li_3Na_3Fe_2F_{12}$. To obtain the value of ζ, we notice that the transition $^4T_1$ to $^6A_1$ has

been reported to be 14200 cm^{-1} in Fe^{3+}:$KMgF_3$[8]. From this, D_q is found to be 1340 cm^{-1} for Fe^{3+}:$KMgF_3$ by using the above values of B, C, and α. These values of B, C, α, and D_q enable us to obtain ζ=371cm^{-1} from the experimental value $a_c = 51.2 \times 10^{-4} cm^{-1}$ of Fe^{3+}:$KMgF_3$[9] (calculated value is $a_c = 51.2 \times 10^{-4} cm^{-1}$).

To justify the above values of B, C, α, and ζ for Fe^{3+}:$RbCdF_3$ and Fe^{3+}:$CsCdF_3$, we use them to calculate the ZFS parameter a_c. Taking $D_q = 1297 cm^{-1}$, a_c is evaluated to be $44.5 \times 10^{-4} cm^{-1}$, which is consistent with the experimental data $a_c = (44.5 \pm 0.2) \times 10^{-4} cm^{-1}$ for Fe^{3+}:$RbCdF_3$ (Ref.[10]). Similarly for Fe^{3+}:$CsCdF_3$, we take $D_q = 1254\,cm^{-1}$ and obtain $a_c = 38.7 \times 10^{-4} cm^{-1}$ in agreement with the observed value $(38.7 \pm 0.3) \times 10^{-4} cm^{-1}$ (Ref.[11]), respectively. It is reasonable that the obtained $D_q = 1254\,cm^{-1}$ of Fe^{3+}:$RbCdF_3$ is smaller than $D_q = 1297\,cm^{-1}$ of Fe^{3+}:$CsCdF_3$, for the bond distance of the former (R_0 = 0.2009nm) is greater than that of the latter ($R_0 = 0.1986$ nm)[11].

The point symmetry changes from O_h to C_{4v} when the Cd^{2+}- vacancy occurs at [001] axis of Fe^{3+}:$RbCdF_3$ and Fe^{3+}:$CsCdF_3$ crystals. As results of this, the crystal field components B_{20} and B'_{40} become nonzero and $D = 0, F = 0$, and $a = a_c$. ZFS parameters D, F, and a are calculated by using the values of D_q and ζ obtained above and B, C, and α given in Ref.[7], and by treating B_{20} and B'_{40} as adjustable parameters. We take $B_{20} = 2600\,cm^{-1}$ and $B'_{40} = 640\,cm^{-1}$ for $RbCdF_3$ and $B_{20} = 2850\,cm^{-1}$ and $B'_{40} = 850\,cm^{-1}$ for $CsCdF_3$. The calculated values for the ZFS parameters are given in Table 1. A good agreemant between theory and experiments can be seen from the table. These values of B_{20} and B'_{40}, which have led to ZFS parameters D, F, and a consistent well with experimental data, can be regarded as reliable.

It is noted that the crystals distort due to the [001] Cd^{2+}-vacancies: A ligand F^- along the [001]-axis moves toward the central metal ion Fe^{3+} by an amount of Δ. Both the distrotion and the Cd^{2+}-vacancy itself contribute to the crystal field ($B_{20} \neq 0$ and $B'_{40} \neq 0$), leading to $D \neq 0$, $F \neq 0$ and $a \neq a_c$. The crystal field contribution will be analysed in detail in next section.

Table 1. The ZFS parameters (in units of cm^{-1}) of Fe^{3+}-V_{Cd} in $RbCdF_3$ and $CsCdF_3$ crystals doped with Fe^{3+}.

	$RbCdF_3$			$CsCdF_3$		
	D	F	a	D	F	a
Reference[1]	-452	35.9	38.0	-490	39.0	37.0
The present work	-427	17.8	37.9	-543.1	19.4	37.5
Experimental[1]	-421.7(1)	18.0(2)	38.2(2)	-547.7(1)	19.5(2)	37.0(2)

The calculated results of Takeuchi *et al.*[1] are also listed in Table 1 for comparison. In the calculation, the authors of Ref. [1] have adopted the superposition model of spin-

Hamiltonian, ignored the effect of the Cd^{2+}-vacancy and taken into account only the contribution of the lattice distortion to the ZFS parameters. They have taken the superposition model parameters (see section IV for details) $\bar{b}_2(0.2027\,\text{nm})$=-0.0850 cm^{-1}, $\bar{b}_4(0.18668\,\text{nm})$= 0.00154 cm^{-1}, $t_2' = 8$, and $t_4' = 14$ for the crystals and the F^--displacement $\Delta = 0.0104$ nm for $RbCdF_3$ and 0.0112 nm for $CsCdF_3$ as well as $R_0 = 0.2011$ and 0.2015 nm for the crystals, respectively. The obtained results for D and a consist well with the experimental data, but the calculated value for F is twice as large as the experimental result. The effect of the Cd^{2+}-vacancy is emphasized in the next section and the superposition model of spin-Hamiltonian is to be discussed in section IV.

Both our fifth-order perturbation formula and the consequent numerical results show that each ZFS parameter depends on all the crystal field parameters: $b_k^q = b_k^q(B_{20}, B_{40}, B_{44})$. It is also important that the dependences are in general nonlinear. This supports the former calculations[5,12].

III. CRYSTAL FIELDS RESULTING FROM THE VACANCY AND DISTORTION

The ZFS arises from the combined interaction of the crystal field H_{cf} and the spin-orbit coupling. The crystal field H_{cf} for Fe^{3+}-V_{Cd} pairs in $RbCdF_3$ and $CsCdF_3$ crystals comes from: 1) the H_{cf}^{p} of cubic symmetry due to the perfect lattice, 2) H_{cf}^{v} of tetragonal symmetry arising from vacancy, and 3) H_{cf}^{d} of tetragonal symmetry resulting from the vacancy-induced lattice distortion. The cubic part H_{cf}^{p}, which is related to the crystal field parameter D_q, has been obtained from the analysis of the ZFS parameter a_c in section II. We now analyse H_{cf}^{v} and H_{cf}^{d} by using the superposition crystal field model for obtaining information about the lattice distortion.

The superposition crystal field model assumes that the crystal field arising from the ligands can be made up superpositionally[3]. With the use of Eg.(4), the crystal field parameters B_{kq} are given as

$$B_{kq} = \sum_j \bar{A}_k(R_j) f_{kq} K_{kq}(\theta_j, \phi_j), \tag{9}$$

where $(R_j, \theta_j.\phi_j)$ denote the coordinate of j-th ligand; $f_{20} = 2$, $f_{40} = 8$, and $f_{44} = 8\sqrt{70}$; K_{kq} are given as[3]

$$\begin{aligned} K_{20} &= \frac{1}{2}(3\cos^2\theta - 1), \\ K_{40} &= \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3), \\ K_{44} &= \frac{35}{8}\sin^4\theta\cos 4\phi. \end{aligned} \tag{10}$$

The intrinsic parameters $\bar{A}_k(R_j)$ depend on R_j and they are given in terms of the power

law[3]

$$\bar{A}_k(R_j) = \bar{A}_k \left(\frac{R_o}{R_j}\right)^{t_k} . \tag{11}$$

In the expression, $\bar{A}_k \equiv \bar{A}_k(R_0)$ and R_0 is a reference distance which is taken as the distance between Fe^{3+} and F^- in a perfect lattice. The power law exponents t_k follow the rule $t_4 > t_2 > 0$[3]. When taking $t_2 = 3$ and $t_4 = 5$, the superposition crystal field model is actually equivalent to the point charge model[3]. We take $t_2 = 5$ and $t_4 = 7$ in our calculation. We note that $\bar{A}_2 \gg \bar{A}_4 > 0$[3]. The $\bar{A}_4$ can be found to relate to the optical parameter D_q by $\bar{A}_4 = 3D_q/4$ for octahedral coordination of cubic symmetry. This relation is approximately applicable for weak distortion. To obtain values of $\bar{A}_2$, we notice that the ratio $\bar{A}_2/\bar{A}_4 \equiv \rho$ tends to be a constant for iron-group ($3d^N$) ions. For instance, ρ has been found to be 10.8[13] for $Co^{2+} - Cl^-$, 10.6 ± 0.3 for $Fe^{2+} - O^{2-}$[14], and 11.3 for $Cr^{3+} - O^{2-}$[15]. We take $\rho = 11$, and from the D_q values obtained in section II we finally obtain the intrinsic parameters for Fe^{3+}–F^- as follows (in cm^{-1}):

$$\begin{aligned} &\bar{A}_2(R_0) = 10700,\ \bar{A}_4(R_0) = 973 \ \text{(for } Fe^{3+} : RbCdF_3); \\ &\bar{A}_2(R_0) = 10346,\ \bar{A}_4(R_0) = 941 \ \text{(for } Fe^{3+} : CsCdF_3). \end{aligned} \tag{12}$$

The two sets of parameters have different values because the crystals have different values of R_0[1].

As an effect of the Cd^{2+}-vacancy at the [001]-axis, a ligand F^- in the direction moves toward the central metal ion Fe^{3+}. Assuming such a displacement is $\Delta (\Delta \ll R_0)$ and using Eqs.(9)–(11), the crystal field components for H_{cf}^{d} are obtained to be

$$\begin{aligned} B_{20} &= 2t_2 \bar{A}_2(R_0) \frac{\Delta}{R_0}, \\ B'_{40} &= 8t_4 \bar{A}_4(R_0) \frac{\Delta}{R_0}. \end{aligned} \tag{13}$$

The effect of the Cd^{2+}-vacancy is equivalent to a negative point charge of $-2 \mid e \mid$ located at the position of the vacancy (which is $2R_0$ from Fe^{3+}), namely, it is equivalent to two F^- ions at the Cd^{2+} position in the perfect lattice. Consequently, the crystal field parameters for H_{cf}^{v} are obtained from Eqs. (9)–(11) to be

$$\begin{aligned} B_{20} &= 2^{2-t_2} \bar{A}_2(R_0), \\ B'_{40} &= 2^{4-t_4} \bar{A}_4(R_0). \end{aligned} \tag{14}$$

The H_{cf}^{d} and H_{cf}^{v} have been evaluated as shown in Table 2 by substituting the results of Eq.(12) as well as $t_2 = 5$ and $t_4 = 7$ into Eqs.(13) and (14). Δ has been taken to be $0.010R_0$ for $RbCdF_3$. It results in $B_{20} = 2408\,cm^{-1}$ and $B'_{40} = 667\,cm^{-1}$, consistent well with $B_{20} = 2600\,cm^{-1}$ and $B'_{40} = 640\,cm^{-1}$ which fit the experimental ZFS data of D, F, and a. Similarly, we have obtained $\Delta = 0.014R_0$ for $CsCdF_3$.

Table 2. The crystal field parameters (in units of cm^{-1}) of $Fe^{3+} - V_{Cd}$ in $RbCdF_3$ and $CsCdF_3$ crystals doped with Fe^{3+}.

	H_{cf}^{d}	H_{cf}^{V}	Total	Fitted[a]
		$RbCdF_3(\Delta = 0.010R_0)$		
B_{20}	1070	1338	2408	2600
B'_{40}	545	122	667	640
		$CsCdF_3(\Delta = 0.014R_0)$		
B_{20}	1448	1293	2741	2850
B'_{40}	738	118	856	850

[a] The values fit the ZFS parameters D, F, and a are shown in Table 1.

It is worthwhile to point out that the calculated results listed in Table 2 are independent of R_0. Its value has been given to be 0.2011 nm for $RbCdF_3$ and 0.2015 nm for $CsCdF_3$[1], the former being comparable to 0.2009 nm reported in Ref.[11]. These allow us to obtain

$$\Delta(RbCdF_3) \cong 0.0020\,\text{nm},$$
$$\Delta(CsCdF_3) \cong 0.0028\,\text{nm}.$$

Our results can be compared with $\Delta(RbCdF_3) \cong 0.0104$ nm and $\Delta(CsCdF_3) \cong 0.0112$ nm obtained in Ref.[1].

The effect of the Cd^{2+}-vacancy has been ignored in Ref.[1]. However, this effect cannot be neglected, as shown in Table 2. Especially, it contributes to B_{20} a value one half of the total value. Obviously, if this effect is ignored, we would not be able to understand the origin of the crystal field. Similar case may happen in other systems. For example, when a $KMgF_3$ crystal is doped with Fe^{3+},Cr^{3+}, or Gd^{3+}, a K^+ site in the [111] direction will be vacant. The K^+-vacancy should be important as well since the distance between it and the central metal ion ($\sqrt{3}R_0$) is smaller than that ($2R_0$) in the present Fe^{3+}-V_{Cd} case.

IV. DISCUSSION

The superposition model established for the crystal field has been extended to analyse the ZFS parameters of S(^{6}S and ^{8}S) -state ions by Newman and coworkers[2,3]. According to them,[3] the assumptions for crystal fields are suitable for ZFS of S-state ions: A ZFS parameter b_k^q arises superpositionally from ligands. Like the crystal field parameter B_{kq}, b_k^q is expressed as

$$b_k^q = \sum_j \bar{b}_k \left(\frac{R_0}{R_j}\right)^{t'_k} K_{kq}(\theta_j, \phi_j), \tag{15}$$

where $K_{kq}(\theta, \phi)$ are given in Eq.(10), $\bar{b}_k \equiv \bar{b}_k(R_0)$ are intrinsic parameters, and for $RbCdF_3$ ($\Delta = 0.010R_0$) the power law exponents follow the rule $t'_4 > t'_2 > 0$. The parameters $\bar{b}_k$ and $t'_k (k = 2, 4, 6)$ are determined adjustably from experimental data.

The superposition model of spin-Hamiltonain establishes the relations among the ZFS

parameters to provide a simple way of analysing experimental EPR data. It does not show the physical process in which the ZFS of ^6S-state ions arises. Let us consider a situation having identical bond lengths ($R = R_j$) of sixfold D_{3d} or fourfold D_{2d}. It follows from Eqs.(9)–(11) and (15) that $b_k^q = \bar{b}_k(R)\sum K_{kq}$ and that $B_{kq} = \bar{A}_k(R)f_{kq}\sum K_{kq}$. The results show that a ZFS parameter b_k^q depends on a crystal field parameter B_{kq} linearly and that it is independent of other crystal field parameters. For a general case, the superposition model includes actually an assumption that b_k^q varies linearly with B_{kq}.

According to the crystal field theroy, the ZFS is a combined effect of the crystal field and the spin-orbit interactions. Therefore, a ZFS paramenter b_k^q must depend on all crystal field parameters $B_{kq}(k = 2, 4, 6; q = -k, 1-k, \cdots, k)$. This point has been verified by the present and previous works[4,5,12]. These works have also shown that the relation between b_k^q and B_{kq} is not a simple linear dependence and that the nonlinear terms are not negligible in general. Obviously, the superposition model is not applicable to cases where the nonlinear terms are not negligible because in such a case the contributions from ligands to the ZFS parameters are not superpositionable.

Although the superposition model of spin-Hamiltonian is inconsistent with the microscopic perturbation theory, it has indeed received a great success in accounting for experimental data of a lot of crystals[3]. It is interesting to investigate the reason from the first principle.

V. CONCLUSION

There are Cd^{2+}-vacancies on [001] axis in the $RbCdF_3$ and $CsCdF_3$ crystals doped with Fe^{3+} impurities. The vacancy induces lattice distortion: A ligand F^- along [001] moves towards the central Fe^{3+} by an amount of Δ. Such a distortion and the vacancy itself contribute to the crystal field and the ZFS of Fe^{3+} ions. The contribution arising from the Cd^{2+}-vacancy cannot be neglected. The value of Δ is calculated to be 0.0020 nm for $RbCdF_3$ and 0.0028 nm for $CsCdF_3$.

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