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Net-charge-compensation effects on the crystal field and the spin Hamiltonian for the Fe^{3+} ions at the K^+-vacancy sites in Fe^{3+}:$KZnF_3$ and Fe^{3+}:$KMgF_3$ crystals

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A microscopic theory is presented for the spin-Hamiltonian (SH) parameters of ${}^6S(d^5)$ ions in trigonal symmetry. This theory establishes the relationships between the SH and the crystal-field (CF) parameters. It enables us to study the net-charge-compensation (NCC) SH effect as a result of the NCC CF contribution for Fe^{3+} ions at the trigonal K^+-vacancy sites in Fe^{3+}:$KZnF_3$. The microscopic contributions to the NCC CF parameters are then investigated, by proposing vacancy-induced lattice-distortion models according to the ENDOR data of Krebs and Jeck. In particular, the vacancy-induced and the distortion-induced dipolar effects are suggested and the former is found important.

I. INTRODUCTION

When paramagnetic impurities Fe^{3+} substitute for the Zn^{2+} ions in $KZnF_3$ crystals, a K^+ ion near the impurity can be vacant owing to the charge compensation, to form a trigonal defect center denoted by V_K.[1] As the most important consequence, trigonal spin Hamiltonian (SH) parameters arise,[1] representing a net-charge-compensation (NCC) contribution.[2,3] Based on the phenomenological superposition SH model,[4] Murrieta *et al.*[5] and Takeuchi, Arakawa, and Ebisu[6] attributed this contribution to the vacancy-induced geometrical change in the ligand configuration. The present paper attempts to provide a microscopic interpretation.

In a microscopic view, SH parameters are a result of crystal-field (CF) and spin-orbit interactions. It is clear that the CF of Fe^{3+} ions at the vacancy sites differs from that at the cubic sites. This difference represents the NCC CF contribution, and it gives rise to the NCC SH parameters. It is apparent that the vacancy-induced lattice distortion makes a contribution to the NCC CF.[7,8] Also, the vacancy itself does so as an effective negative charge in a perfect cubic lattice.[8] In addition, as will be shown in the present work, multipolar moments are induced at the sites of neighboring closed-shell ions by vacancy and vacancy-induced lattice distortion, making another important contribution. All of these will be taken into account in the present study of the NCC CF and SH effects.

II. MICROSCOPIC THEORY OF SPIN-HAMILTONIAN PARAMETERS

We are concerned with the Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{\mathrm{CF}}+\mathcal{H}_{\mathrm{s.o.}} \; . \tag{1}$$

Terms on the right side denote the electrostatic, CF, and spin-orbit Hamiltonians, respectively. The spin-spin interaction has been found to be negligible in affecting the SH parameters of ${}^6S(3d^5)$ ions;[9] it is omitted in the present work. For Fe^{3+}-V_K, the CF Hamiltonian is written as[8,10] $(C_{3v}, z\|\langle 111\rangle)$

$$\mathcal{H}_{\mathrm{CF}}=B_{20}C_0^{(2)}+B_{40}C_0^{(4)}+B_{43}(C_3^{(4)}-C_{-3}^{(4)}) \; , \tag{2}$$

where $C_q^{(k)}$ are Wybourne-normalized spherical harmonics. It is convenient to define[8,10] $Dq=-\frac{1}{28}(B_{40}+\sqrt{7/10}B_{43})$ and $B'_{40}=B_{40}-\sqrt{7/10}B_{43}$ so that B_{20} and B'_{40} vanish identically in cubic symmetry. The parameters B_{20}, B'_{40}, and Dq' represent the NCC CF contribution,[8] where $Dq'=Dq-Dq_c$, with Dq_c denoting the Dq value of the cubic center.

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

$$\mathcal{H}_s=\tfrac{1}{3}b_2^0O_2^0+\tfrac{1}{60}(b_4^0O_4^0+b_4^3O_4^3) \; , \tag{3}$$

where $O_k^q=O_k^q(S_x,S_y,S_z)$ are Stevens operators. The SH parameters b_k^q can be expressed in terms of the matrix elements of $\mathcal{H}_s$ within the ground states $|S,M_s\rangle$:

$$\begin{aligned} b_2^0&=\tfrac{1}{28}[5\langle\tfrac{5}{2},\tfrac{5}{2}|\mathcal{H}_s|\tfrac{5}{2},\tfrac{5}{2}\rangle-\langle\tfrac{5}{2},\tfrac{3}{2}|\mathcal{H}_s|\tfrac{5}{2},\tfrac{3}{2}\rangle\\ &\qquad -4\langle\tfrac{5}{2},\tfrac{1}{2}|\mathcal{H}_s|\tfrac{5}{2},\tfrac{1}{2}\rangle] \; ,\\ b_4^0&=\tfrac{1}{14}[\langle\tfrac{5}{2},\tfrac{5}{2}|\mathcal{H}_s|\tfrac{5}{2},\tfrac{5}{2}\rangle-3\langle\tfrac{5}{2},\tfrac{3}{2}|\mathcal{H}_s|\tfrac{5}{2},\tfrac{3}{2}\rangle\\ &\qquad +2\langle\tfrac{5}{2},\tfrac{1}{2}|\mathcal{H}_s|\tfrac{5}{2},\tfrac{1}{2}\rangle] \; ,\\ b_4^3&=(2\sqrt{10})\langle\tfrac{5}{2},\tfrac{5}{2}|\mathcal{H}_s|\tfrac{5}{2},-\tfrac{1}{2}\rangle \; . \end{aligned} \tag{4}$$

It is convenient to use notations D, F, and a, which are related to b_k^q by[3] $D=b_2^0$, $F=3b_4^0-(3/20\sqrt{2})b_4^3$, and $a=-(3/20\sqrt{2})b_4^3$. D and F vanish identically in cubic symmetry. Thus D, F, and a' represent the NCC SH contribution,[2,3] where $a'=a-a_c$, with a_c denoting the value of a for the cubic center.

Various perturbation procedures have been suggested to approach the SH parameters of ${}^6S(d^5)$-state ions during the past decades (see Refs. 10–13 and references therein). In this work, we adopt that proposed recently by Yu and Rudowicz:[13] $\mathcal{H}_0+\mathcal{H}_{\mathrm{CF}}$ are treated as the unperturbed Hamiltonian and $\mathcal{H}_{\mathrm{s.o.}}$ as the perturbation term. In this perturbation procedure, the spin-orbit coupling acts as an effective Hamiltonian

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TABLE I. SH parameter b_2^0 (in units of 10^{-4} cm^{-1}) of Mn^{2+} ions calculated by taking $B=911$ cm^{-1}, $C=3273$ cm^{-1}, $\alpha=65$ cm^{-1}, $\zeta=337$ cm^{-1}, $B_{20}=-1000$ cm^{-1}, and $B'_{40}=1000$ cm^{-1}.

	Present work			Previous works	
Dq (cm^{-1})	$b_2^{0(2)}$	$b_2^{0(3)}$	b_2^0(total)	b_2^0(BO)[a]	b_2^0(W)[b]
500	55	13	68	60	68
600	67	13	80	75	81
700	80	14	94	91	93
800	94	14	108	108	107
900	109	15	124	130	123
1000	125	16	141	153	138
1100	143	17	160	180	154
1200	163	18	181	214	171

[a] Lowest- (third-) order results for the Blume-Orbach procedure (Ref. 15).

[b] Lowest- (fourth-) and next-lowest (sixth-) order results for the Watanabe procedure (Refs. 10, 16).

$$\mathcal{H}_{\text{eff}}=\mathcal{H}_{\text{s.o.}}+\sum_n \frac{|\mathcal{H}_{\text{s.o.}}|n\rangle\langle n|\mathcal{H}_{\text{s.o.}}|}{E(^6S)-E(n)}+\cdots \tag{5}$$

operating on the ground states $|S,M_s\rangle$, where $|n\rangle$ denotes excited states obtained by diagonalizing $\mathcal{H}_0+\mathcal{H}_{\text{CF}}$. The *effective* Hamiltonian [Eq. (3)] is thus correlated with the *true* Hamiltonian [Eq. (1)] by replacing $\mathcal{H}_s$ in Eq. (4) with $\mathcal{H}_{\text{eff}}$ given by Eq. (5). Consequently, we obtain

$$b_k^q=b_k^q(B,C,\alpha,B_{20},B'_{40},Dq,\zeta) \tag{6}$$

$$=\sum_m b_k^{q(m)}\,, \tag{7}$$

where B and C are the Racah parameters, α the Trees correction, ζ the spin-orbit interaction constant, and $b_k^{q(m)}$ the contribution of the mth order. It follows from Eq. (5) that $b_k^{q(m)}\propto\zeta^m$; it is easy to show $m\geq k$.[13] Equation (5) displays explicit expressions of the first and second orders. Our calculations are carried out up to sixth order and by taking into account all states in the $3d^5$ configuration. This is achieved by a FORTRAN program. A copy of the program can be obtained from the author upon request.

The calculation results for b_2^0 of Mn^{2+} ions are compared to those[14] using the earlier published expressions[10,15,16] in Table I. We have taken Dq up to 1200 cm^{-1}, compared to $Dq=1200$ cm^{-1} obtained[17] for Mn^{2+}:MgO from optical spectra.[18] A consistency can be seen among the results. The results for b_4^0 and b_4^3 of Fe^{3+} ions are given in Tables II and III, respectively. The values of Dq have been assumed up to 1500 cm^{-1}, compared to $Dq=1510$ cm^{-1} found in Fe^{3+}:Al_2O_3.[19,20] These tables indicate that b_k^q arises mainly from the kth-order effect of the spin-order coupling, with an important correction resulting from the next order, as has been pointed out previously.[13] In Tables II and III, the results obtained by including and excluding the spin doublets have been listed separately. It is seen that these states make predominant contributions to the rank-4 SH parameters, similar to the cubic case.[17,21] These states, however, cannot affect the SH parameters at the second and third orders. In other words, the second-to-third-order contributions to b_2^0 result entirely from the spin quartets. Thus Table I indicates the negligible role of the spin doublets in affecting this parameter. Tables I–III show the good convergency of the perturbation series.

The dependences of the SH parameters on the CF ones are plotted in Figs. 1–3, for D, F, and a, respectively. Similar to the tetragonal case,[13] every CF parameter has contributions to each SH parameter; F and a depend on B_{20} and B'_{40} almost linearly, and b_2^0 is sensitive to B'_{40}, but not so to B_{20}. Different from the case of tetragonal symmetry, however, B_{20} and B'_{40} are both important in their contributions to the rank-4 parameters F and a. Further, in tetragonal symmetry the low-symmetric CF

TABLE II. SH parameter b_4^0 (in units of 10^{-4} cm^{-1}) of Fe^{3+} ions calculated by taking $B=900$ cm^{-1}, $C=3300$ cm^{-1}, $\alpha=70$ cm^{-1}, $\zeta=400$ cm^{-1}, $B_{20}=5000$ cm^{-1}, and $B'_{40}=5000$ cm^{-1}.

	Including spin doublets				Excluding spin doublets
Dq (cm^{-1})	$b_4^{0(4)}$	$b_4^{0(5)}$	$b_4^{0(6)}$	b_4^0(total)	b_4^0(total)
800	−7.1	−0.6	−0.0	−7.7	−0.5
900	−9.4	−0.7	−0.0	−10.1	−0.6
1000	−12.3	−1.0	−0.1	−13.3	−0.7
1100	−16.3	−1.3	−0.1	−17.7	−0.8
1200	−21.8	−1.7	−0.2	−23.7	−0.9
1300	−29.7	−2.3	−0.3	−32.3	−1.0
1400	−41.2	−3.3	−0.4	−44.9	−1.1
1500	−58.9	−4.8	−0.7	−64.4	−1.3

TABLE III. SH parameter b_4^3 (in units of 10^{-4} cm^{-1}) of Fe^{3+} ions calculated by taking $B=900$ cm^{-1}, $C=3300$ cm^{-1}, $\alpha=70$ cm^{-1}, $\zeta=400$ cm^{-1}, $B_{20}=5000$ cm^{-1}, and $B'_{40}=5000$ cm^{-1}.

	Including spin doublets				Excluding spin doublets
Dq (cm^{-1})	$b_4^{3(4)}$	$b_4^{3(5)}$	$b_4^{3(6)}$	b_4^3(total)	b_4^3(total)
800	−65	−26	−1	−92	8
900	−94	−33	−1	−128	10
1000	−134	−42	−1	−176	12
1100	−186	−54	−2	−242	15
1200	−259	−71	−3	−332	19
1300	−361	−95	−4	−460	24
1400	−507	−133	−6	−645	30
1500	−722	−192	−10	−924	39

components contribute the value a_t to the parameter a, which is related to F by the relation $F/a_t \approx -(0.2-0.5)$.[13,22] This relation does not work in trigonal symmetry.

Combination of Eqs. (4) and (5) establishes relationships between the SH and CF parameters for a $^6S(3d^5)$ ion in trigonal symmetry. This makes it possible to derive CF parameters from the experimental SH data for the Fe^{3+}-V_K centers in KZnF$_3$. By taking $B=877.5$, $C=3146.5$, $\alpha=64.5$, and $\zeta=371$ cm^{-1} (Ref. 13), we adjust the CF parameters to fit to the experimental data reported by Krebs and Jeck.[1] The results are shown in Table IV, together with those for the cubic cases.[13,23] A similar calculation is worked out for the Fe^{3+}-V_K centers in KMgF$_3$ (observed data from Refs. 2 and 24), and the results are listed in Table IV for comparison.

III. CRYSTAL-FIELD MODELS

We consider a crystal field as a sum of the electrostatic (EL) contribution and the effective covalence-overlap (CO) one to write

$$B_{kq}=B_{kq}(\mathrm{EL})+B_{kq}(\mathrm{CO})\ . \tag{8}$$

According to Faucher and Garcia, $B_{kq}(\mathrm{EL})$ is given as[25]

$$B_{kq}(\mathrm{EL})=(-1)^{q+1}e\langle r^k\rangle \sum_J \sum_n \mathbf{M}_J^{(n)}\cdot\nabla_J^{(n)}\left[\frac{C_{-q}^{(k)}(\mathbf{r}_J)}{|\mathbf{r}_J|^{k+1}}\right] . \tag{9}$$

In this expression, $\langle r^k\rangle$ is the expectation value for the orbit of open-shell electrons of the paramagnetic ion lo-

TABLE IV. CF and SH parameters of Fe^{3+}-cubic and Fe^{3+}-V$_K$ centers in KZnF$_3$ and KMgF$_3$.

	KZnF$_3$	KMgF$_3$
$T(K)$	300	300
Dq_c (cm^{-1}) (Ref. 13)	1348	1340
a_c (10^{-4} cm^{-1})	52.7(2)	51.2(5)
R (Å) (Ref. 28)	1.982	1.986
B_{20} (cm^{-1})	750	800
B'_{40} (cm^{-1})	350	330
Dq' (cm^{-1})	−44	−93

	D	F (10^{-4} cm^{-1})	a	D	F (10^{-4} cm^{-1})	a
Second order	130.3			112.6		
Third order	−25.1			−25.2		
Fourth order	−0.1	−4.1	38.5	−0.1	−3.5	31.9
Fifth order	−0.2	0.2	6.9	−0.2	0.2	5.8
Sixth order	0.0	0.0	0.4	0.0	0.0	0.3
Total	105.0	−3.9	45.8	87.2	−3.4	38.0
a	106	+1.1	40.1	81.7	+4.2	45.3
b	103	+2.1	47.1			
Expt.	103.4(3)	−3.9(4)	45.6(4)	87.2(5)	−3.3(3)	37.8(3)
Refs.		1			5	

[a] Superposition-model results obtained in Ref. 5. $\bar{b}_2(R=2.027\ \text{Å})=-0.089$ cm^{-1} and $\bar{b}_4$ (1.8668 Å)$=0.001\,54$ cm^{-1} for both crystals, and $R=2.027$ Å, $\alpha=2.8°$, and $\beta=1.1°$ for KZnF$_3$ and $R=1.993$ Å, $\alpha=6.4°$, and $\beta=4.8°$ for KMgF$_3$.

[b] Superposition-model results obtained in Ref. 6. $\bar{b}_2(R=1.950\ \text{Å})=-0.1160$ cm^{-1} and $\bar{b}_4(1.950\ \text{Å})=0.00084$ cm^{-1}, $R_1=R_2=1.981$ Å, $\alpha=2.9°$, and $\beta=1.5°$.

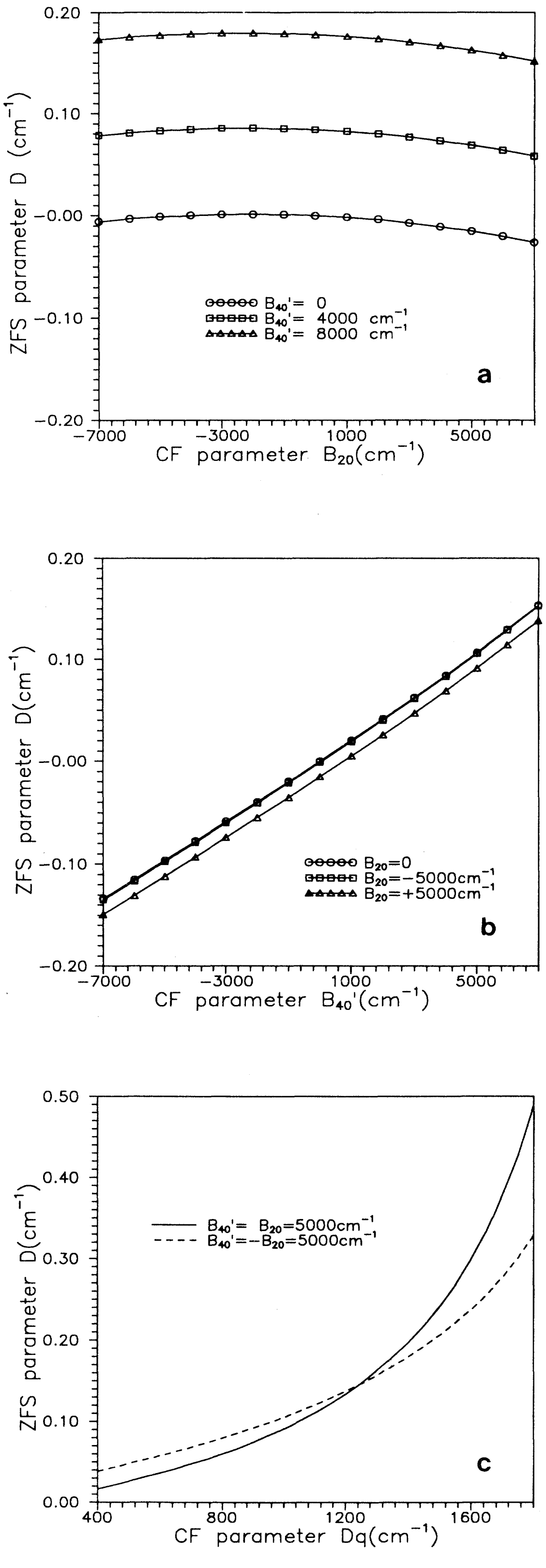

FIG. 1. SH parameter b_2^0 of an Fe^{3+} ion in trigonal symmetry, as a function of (a) B_{20}, (b) B'_{40}, and (c) Dq. $B=900$ cm^{-1}, $C=3300$ cm^{-1}, and $\zeta=400$ cm^{-1}; $Dq(a)=Dq(b)=1000$ cm^{-1}.

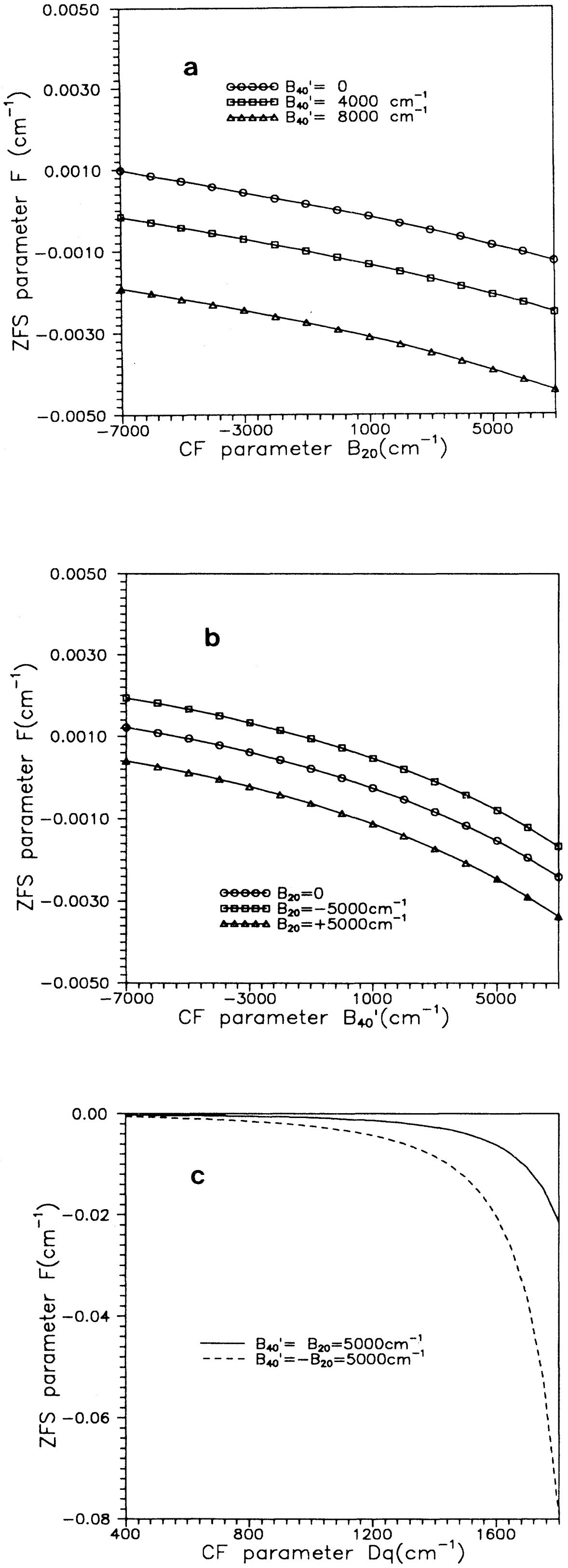

FIG. 2. F of Fe^{3+} as a function of (a) B_{20}, (b) B'_{40}, and (c) Dq. Parameter values are used the same as in Fig. 1.

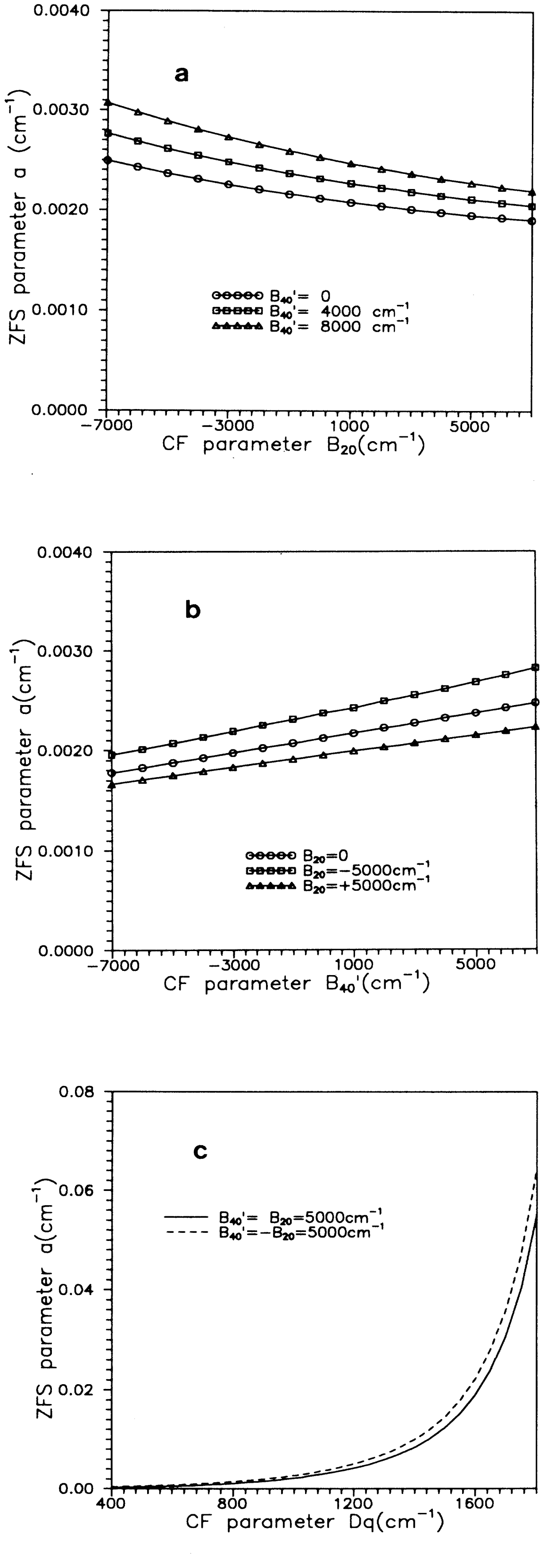

FIG. 3. a of Fe^{3+} as a function of (a) B_{20}, (b) B'_{40}, and (c) Dq. Parameter values are used the same as in Fig. 1.

cated at the origin of the coordinate system; $\mathbf{r}_J$ denotes the coordinate of the Jth neighboring ion; $M_J^{(0)}$, $M_J^{(1)}\equiv\mathbf{M}_J$, and $M_J^{(2)}$ are monopolar, dipolar, and quadrupolar moments, respectively, of the Jth ion; the summation is taken over all ions in the crystal. The monopolar moments are taken as the valence charges. Neglecting the quadrupolar contribution, the dipolar moments are given as[25]

$$\mathbf{M}_J=\alpha_J\sum_{J'}\nabla_{J'}\left[\frac{M_{J'}^{(0)}}{|\mathbf{r}_{J'}-\mathbf{r}_J|}-\frac{\mathbf{M}_{J'}\cdot(\mathbf{r}_{J'}-\mathbf{r}_J)}{|\mathbf{r}_{J'}-\mathbf{r}_J|^3}\right], \qquad (10)$$

where α_J is the dipole polarizability of the Jth closed-shell ion. This equation is written for each ion's site and for each of the three dipolar moment components to yield a linear system in the unknown moment components. A self-consistent calculation[25] is necessary to determine the dipolar moment components by resolving the linear equations given by Eq. (10). The rank of the linear system is in general infinite, but it becomes finite for crystals having translational symmetry.[25] The quadrupolar effect is omitted in our calculations owing to the small polarizabilities of K^+, Zn^{2+}, and F^- ions.[26]

Concerning the effective covalence-overlap contribution, the empirical power law has been shown to be valid for Dq:[27]

$$Dq(\mathrm{CO})=AR^{-n}, \qquad (11)$$

with A denoting a constant independent of R, the metal-ligand distance. The exponent n has been obtained to be 3–6, depending on magnetic ion, ligand, coordination, and the calculation method (see Ref. 27 and references therein). We take $n=5$ and R the mean value of the Fe^{3+}-F^- distances.

A. Cubic sites

A perfect $KZnF_3$ crystal is of O_h symmetry. This symmetry retains for the Zn^{2+} and K^+ sites, while the F^- sites possess D_{4h} symmetry. A group-theory consideration[25] shows that the lattice-induced dipolar moments[25] at the sites of K^+, Zn^{2+}, and F^- are all zero in the crystal.

When an impurity Fe^{3+} substitutes for a Zn^{2+} ion, the dipolar moments at every site of the closed-shell ions become nonzero because of the decrease in symmetry. The main origin of the dipolar moments comes from the extra charge of the impurity, called the "impurity-induced" dipolar effect. Another source comes from the impurity-induced lattice distortion.[28] Because of the lack of translational symmetry due to the presence of the impurity, the dimension of the linear equations (10) concerning the dipolar moment components is infinite. Therefore a proper approximation has to be assumed by omitting ions far away from the impurity. Our calculation takes a size of 7^3 unit cells with Fe^{3+} located at the center. This involves 5142 dipolar moment components in the self-consistent calculation. We obtain the following results for $Dq_c(\mathrm{EL})$: monopolar, 138.5 cm^{-1}; dipolar, 56.7 cm^{-1}, total, 195.2 cm^{-1}. The following parameter values have been used in the calculations: $\alpha(K^+)=0.827$ Å^3,

$\alpha(\mathrm{Zn}^{2+})=0.676$ Å^3, and $\alpha(\mathrm{F}^-)=0.731$ Å^3 as the self-consistent *ab initio* values of polarizabilities,[26] $\langle r^2\rangle_{3d}=1.414$ a.u. and $\langle r^4\rangle_{3d}=2.765$ a.u. as the self-consistent *ab initio* values of expectation values of 3*d* orbital of Fe^{3+} (Ref. 29), $a_0=4.054$ Å as the unit-cell crystallographic parameter, and $R=1.982$ Å.[28] The impurity-induced dipolar effect yields a contribution of 45.2 cm^{-1} to Dq_c. Comparison of $Dq_c(\mathrm{EL})=195.2$ cm^{-1} with $Dq_c(\mathrm{expt})=1348$ cm^{-1} (Ref. 13) indicates $Dq(\mathrm{CO})=1152.8$ cm^{-1}, leading to $A=35\,360$ cm^{-1} Å^5 according to Eq. (11).

B. Trigonal sites

The CF of Fe^{3+} ions at the K vacancy sites in KZnF_3 differs from that at the cubic sites. The difference is measured by the NCC CF parameters B_{20}, B'_{40}, and Dq'. The physics in the problem is similar to, but more complicated than, the cubic case. First, the absence of the K^+ ion at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ serves effectively as a negative charge of $-e$ in the perfect cubic lattice. It will give an electrostatic contribution.[8] Further, it causes a distortion of the crystalline structure.[1] This distortion must affect the NCC CF.[7,8] Furthermore, it will induce dipolar moments, making a "vacancy-induced" dipolar contribution. Finally, the lattice distortion induced by the vacancy will give rise to another dipolar moment, resulting in a "distortion-induced" dipolar contribution to the NCC CF parameters. All of these will be taken into account.

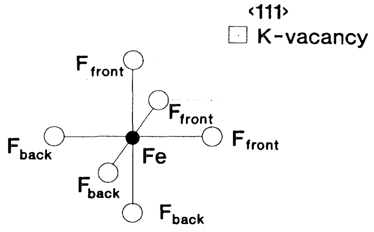

FIG. 4. Local configuration of Fe^{3+}: KZnF_3.

The only information concerning the lattice distortion have been gained from electron-nuclear double-resonance (ENDOR) experiments by Krebs and Jeck.[1] They have found that the three ligand F^- ions in front of the K^+ vacancy rotate outwards by an angle $\alpha=2.8°\pm0.3°$ and that the three F^- ions in back of the vacancy rotate inwards by $\beta=1.1°\pm0.3°$ (see Fig. 4).[1] According to these data, we suppose the "front" and "back" F^- ions to move outwards from the vacancy along the lines joining them by δ_1 and δ_3, respectively, and the central magnetic impurity to move toward the vacancy by δ_2. There are infinite choices for the values of δ_1, δ_2, and δ_3 to fit to the experimental data $\alpha=2.8°\pm0.3°$ and $\beta=1.1°\pm0.3°$. Among them, we take $\delta_1=0.0288R$, $\delta_2=0.0239\pm0.006R$, and $\delta_3=0$ as model I and $\delta_1=0.0346R$, $\delta_2=0.017\pm0.006R$, and $\delta_3=0.010R$ as model II, where $R=1.982$ Å.[28]

TABLE V. NCC contributions to the CF and SH parameters of Fe^{3+}-V_K centers in KZnF_3.

			Model I				Model II	
δ_1/R			0.0288				0.0346	
δ_2/R			0.0239±0.0060				0.017±0.006	
δ_3/R			0				0.010	
CF (cm^{-1})		B_{20}	B'_{40}	Dq'		B_{20}	B'_{40}	Dq'
monopolar								
K^+ vacancy		858	47	−1.6		858	47	−1.6
Distortion[a]		−634	104	−2.8		−624	102	−5.5
dipolar[b]								
V_K induced		−659	70	−4.1		−659	70	−4.1
Distortion induced[a]		28	25	+0.3		−30	25	−1.9
covalence-overlap								
				−3.9				−27.1
total								
a,b,c		−408(65)	267(25)	−14.5(5)		−414(65)	263(25)	−42.2(5)
b,d		−377(65)	244(25)	−14.7(5)		−368(65)	237(25)	−42.7(5)
Fitted[e]		+750	+350	−44		+750	350	−44
SH (10^{-4} cm^{-1})	D	F	a	a'	D	F	a	a'
a,b	77(7)	−0.1(1)	51.3	−1.4(1)	75(6)	−0.1(1)	46.7	−6.0(1)
b,d	71(6)	−0.1(1)	51.2	−1.5(1)	67(5)	−0.1(1)	46.6	−6.1(1)
Expt. (300 K)[f]	103.4	−3.9	45.6	−7.1	103.4	−3.9	45.6	−7.1

[a] Crystalline distortion of distant neighbors omitted.

[b] Self-consistent calculation values.

[c] The total value is obtained by considering simultaneously the four sources contributing to the CF parameters; thus, it is not equal simply to the sum of the individual terms because these sources are related to each other.

[d] Crystalline distortion of distant neighbors taken into account.

[e] See Table IV.

[f] Reference 1.

The self-consistent CF results obtained using these two distortion models are given in Table V. It is noted that the V_K-induced dipolar contribution depends on lattice distortion. However, the values of this contribution listed in Table V are obtained by omitting the lattice distortion. Similarly, the values of the distortion-induced dipolar contribution are obtained by assuming no vacancy. It is seen that the distortion-induced dipolar contribution is negligible. However, the remaining three mechanisms are all important, including the monopolar effect of the vacancy, the vacancy-induced dipolar moments, and the monopolar contribution of the lattice distortion. In particular, the monopolar effect of the vacancy is the only source making a positive contribution to B_{20}. The value of this parameter becomes negative, opposite in sign to the fitted value, owing to the large and negative contributions resulting from the distortion and vacancy-induced dipolar moments. The total electrostatic contribution is about 70% of the fitted value for B'_{40}, which mainly determines the value of b_2^0. These cases do not change with the distortion model adopted. A value of the parameter Dq' is obtained which is rather small in magnitude in model I is improved greatly in model II.

The SH parameters are calculated by taking the obtained CF parameters, as well as $B=877.5\ \text{cm}^{-1}$, $C=3146.5\ \text{cm}^{-1}$, $\alpha=64.5\ \text{cm}^{-1}$, and $\zeta=371\ \text{cm}^{-1}$.[13] The results, as listed in Table V, are consistent with the experimental data for D and a', but not so for F.

It is noted that the distant neighboring ions will displace from their original positions as the nearest neighbors do, making additional contributions to the CF and SH parameters. To study the effect of these unknown displacements, we suppose that the F^- ions nearest to the vacancy move in the same way as the front F^- ions do and that the Zn^{2+} ions near the vacancy move in the same way as the impurity does. The results obtained under these assumptions are given in Table V. There is a little change in the values of F and a'. (It should be pointed out that the calculated magnitudes of F listed in Table V are too small to be reliable, although we believe the negative signs are correct.)

The CF results depend on the Fe^{3+}-F^- distance R in an approximate way, $B_{kq} \propto R^{-(k+1)}$, $R=1.982$ Å, according to Rubio, Murrieta, and Aguilar.[28] It is calculated that the results for the CF and SH parameters do not change greatly with varying values of R in the range $1.95 < R < 2.00$ Å.

A superposition-model analysis[5] of the SH data of the Fe^{3+}-V_K center in $KZnF_3$ assumed a lattice distortion model different form those taken in the present work. The front F^- ions were assumed to move along lines joining them and the vacancy, the back F^- ions to move along lines joining these ions, and the K^+ ion at $(-\frac{1}{2},-\frac{1}{2},-\frac{1}{2})$, and the central impurity not to move. Using different values of the superposition-model parameters,[4] recent analysis[6] has assumed that the front and back F atoms rotate outwards and inwards, respectively, keeping the Fe^{3+}-ligand distances unchanged from $R=1.981$ Å. The results[5,6] obtained by these two groups are listed in Table IV.

IV. CONCLUSIONS

We have presented a microscopic theory for the SH parameters of $^6S(d^5)$ ions in trigonal symmetry. It has been shown that b_k^q arises predominantly from the kth- and $(k+1)$th-order perturbation of the spin-orbit interaction. The spin doublets play a negligible role in contributing to the rank-2 parameter, but they make main contributions to the rank-4 terms. These conclusions are expected to hold for other symmetries.

The theory establishes relationships between the SH and CF parameters. It enables us to derive the values of the NCC CF parameters from the experimental SH data for Fe^{3+}-V_K centers in $KZnF_3$. Microscopic origins contributing to the NCC CF parameters are investigated. In particular, the vacancy-induced and distortion-induced dipolar effects are suggested and the former has been found to be important. The electrostatic model has been shown to be successful in predictions of B'_{40}, but not so for B_{20}.

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