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Analytical expressions for zero-field splittings of $3d^5$ ions in low-symmetry fields and their applications

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Analytical expressions for calculating the electron paramagnetic resonance parameters D, a, and F are developed using a complete diagonalization procedure for $3d^5$ ions in a low-symmetry field. As illustrations, the formulas have been applied to RbCdF:Mn^{2+}, $RbMnF_3$:Mn^{2+}, Rb_2CdF_4:Mn^{2+}, and α-Al_2O_3:Fe^{3+}. Calculations indicate that the optical and EPR spectra for Mn^{2+} ions in $RbCdF_3$, $RbMnF_3$, Rb_2CdF_4, and Fe^{3+} ions in α-Al_2O_3 can be interpreted uniformly.

I. INTRODUCTION

The spin-Hamiltonian (SH) rank-4 parameters a and F as well as the rank-2 parameters D and E are important in describing electron paramagnetic resonance (EPR) spectra for $3d^5$ ions in low-symmetry fields. During recent decades some work[1-3] has been devoted to study of the rank-2 parameters, but only a few papers deal with the calculation of the cubic rank-4 parameter a,[4-7] especially in the case of low symmetry in the framework of a complete diagonalization procedure (CDP). Because of the complexity of the problem, some approximations were used in earlier works.[2]

To fill this gap, in this work we develop analytical expressions of the zero-field splitting (ZFS) parameters D, a, and F for low symmetry. Calculations indicate that the optical and EPR spectra for the Mn^{2+} ions in $RbCdF_3$, $RbMnF_3$, and Rb_2CdF_4, and the Fe^{3+} ions in α-Al_2O_3 can be interpreted uniformly.

II. D_4' (C_{4v}', D_{2d}') SYMMETRY

A. Analytical expression for ZFS parameters

The Hamiltonian including the electron-electron repulsion, the spin-orbit interaction, and the crystal-field potential is given by

$$H = H_e + H_{\mathrm{SO}} + H_{\mathrm{cf}} , \tag{1}$$

where

$$H_e = \sum_i [-(\hbar^2/2m)\nabla_i^2 - Ze/r_i] + \sum_{i>j} e^2/r_{ij} + \text{Trees correction} + \text{Racah correction} , \tag{2}$$

$$H_{\mathrm{SO}} = \sum_i \xi_d S_i L_i , \tag{3}$$

$$H_{\mathrm{cf}} = \sum_{k,q} B_{kq} C_q^{(k)} . \tag{4}$$

The B_{kq} appearing in Eq. (4) are crystal-field parameters and $C_q^{(k)}$ the tensor operators. All other symbols appearing in Eqs. (2) and (3) have their usual meanings.

The irreducible representations of the double group C_2' arising from the $3d^5$ configuration are Γ_3 and Γ_4, involving a 126×126 matrix. This matrix is a function of the electrostatic parameters B and C, the Trees and Racah parameters α and β, the spin-orbit constant ξ_d, and the crystal-field parameters B_{20}, B_{22}, B_{2-2}, B_{40}, B_{44}, B_{4-4}, B_{42}, and B_{4-2}.

In the case of the double group D_4' (C_{4v}', D_{2d}'), the matrix consists of two blocks of dimensions 62 and 64 which belong to the irreducible representations Γ_6 and Γ_7 (see Ref. 2), respectively. The irreducible basis functions and the Hamiltonian matrix are deposited in the AIP's Physics Auxiliary Publication Service.[8]

Following the SH method, the zero-field Hamiltonian in tetragonal symmetry is given by[9-11]

$$\begin{aligned} H = {} & D[S_z^2 - S(S+1)/3] \\ & + (a/6)[S_x^4 + S_y^4 + S_z^4 - S(S+1)(3S^2+3S-1)/5] \\ & + (F/180)[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 \\ & \qquad - 6S(S+1) + 3S^2(S+1)^2] . \end{aligned} \tag{5}$$

Solving the secular equations, the following eigenenergies $E(m_s)$ and corresponding eigen-vectors $|\psi\rangle$ are obtained:

$$E(\pm\tfrac{1}{2}) = a + 2F/3 - 8D/3 , \tag{6}$$

$$|\Psi_1\rangle = |\pm\tfrac{1}{2}\rangle ,$$

$$E(\pm\tfrac{3}{2}) = -\tfrac{1}{2}(a + 2F/3) + 4D/3 - [(a + 2F/3 + 2D)^2 + 5a^2/4]^{1/2} , \tag{7}$$

$$|\Psi_2\rangle = -\cos\alpha|\pm\tfrac{3}{2}\rangle + \sin\alpha|\pm\tfrac{5}{2}\rangle ,$$

$$E(\pm\tfrac{5}{2}) = -\tfrac{1}{2}(a + 2F/3) + 4D/3 + [(a + 2F/3 + 2D)^2 + 5a^2/4]^{1/2} , \tag{8}$$

$$|\Psi_3\rangle = \cos\alpha|\pm\tfrac{5}{2}\rangle + \sin\alpha|\pm\tfrac{3}{2}\rangle ,$$

where

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$$\tan 2\alpha = \frac{\sqrt{5}a/2}{a+2F/3+2D} \ . \tag{9}$$

Hence we have

$$\begin{aligned}\Delta_1 &= E(\pm\tfrac{5}{2}) - E(\pm\tfrac{1}{2}) \\ &= -\tfrac{3}{2}(a+2F/3)+4D \\ &\quad +(a+2F/3+2D)(1+\tan^2 2\alpha)^{1/2} \ ,\end{aligned} \tag{10}$$

$$\begin{aligned}\Delta_2 &= E(\pm\tfrac{3}{2}) - E(\pm\tfrac{1}{2}) \\ &= -\tfrac{3}{2}(a+2F/3)+4D \\ &\quad -(a+2F/3+2D)(1+\tan^2 2\alpha)^{1/2} \ .\end{aligned} \tag{11}$$

Solving Eqs. (6)–(11), we obtain

$$D = \tfrac{1}{28}[2(\Delta_1+\Delta_2)+3(\Delta_1-\Delta_2)/(1+\tan^2 2\alpha)^{1/2}] \ , \tag{12}$$

$$a+2F/3 = \tfrac{1}{7}[2(\Delta_1-\Delta_2)/(1+\tan^2 2\alpha)^{1/2}-(\Delta_1+\Delta_2)] \ , \tag{13}$$

$$a = (\tfrac{1}{5})^{1/2}(\tan 2\alpha)[(\Delta_1-\Delta_2)/(1+\tan^2 2\alpha)^{1/2}] \ . \tag{14}$$

In the SH approximation, the effective spin ground state approximately equals $|\frac{5}{2}\rangle$. However, it is an admixture of $|\frac{5}{2}\rangle$, $|\frac{3}{2}\rangle$, and $|\frac{1}{2}\rangle$ states in the framework of CDP (complete diagonalization procedure). In fact, the CDP ground state is given by

$$\begin{aligned}|\tfrac{5}{2}\rangle(\mathrm{CDP}) &= a_1|{}^6S,\tfrac{5}{2}\rangle + a_2|{}^6S,-\tfrac{3}{2}\rangle \\ &\quad + \text{smaller contributions arising from the } S=\tfrac{3}{2} \text{ and } S=\tfrac{1}{2} \text{ states} \ .\end{aligned} \tag{15}$$

As an equivalent approximation,

$$\begin{aligned}|\tfrac{5}{2}\rangle(\mathrm{CDP}) &\simeq a_1/(a_1^2+a_2^2)^{1/2}|{}^6S,\tfrac{5}{2}\rangle \\ &\quad + a_2/(a_1^2+a_2^2)^{1/2}|{}^6S,-\tfrac{3}{2}\rangle \ .\end{aligned} \tag{16}$$

Here the factor $1/(a_1^2+a_2^2)^{1/2}$ is the normalization constant ($\langle\frac{5}{2}|\frac{5}{2}\rangle=1$).

By means of the approximate equivalence between the SH and CDP,

$$\cos\alpha \simeq a_1/(a_1^2+a_2^2)^{1/2} \ , \tag{17}$$

$$\sin\alpha \simeq a_2/(a_1^2+a_2^2)^{1/2} \ . \tag{18}$$

Hence the following analytical expressions are obtained:

$$T \equiv \tan 2\alpha = \frac{2a_1a_2}{a_1^2-a_2^2} \ , \tag{19}$$

$$D = \tfrac{1}{28}[2(\Delta_1+\Delta_2)+3(\Delta_1-\Delta_2)/(1+T^2)^{1/2}] \ , \tag{20}$$

$$a+2F/3 = \tfrac{1}{7}[2(\Delta_1-\Delta_2)/(1+T^2)^{1/2}-(\Delta_1+\Delta_2)] \ , \tag{21}$$

$$a = (\tfrac{1}{5})^{1/2}T(\Delta_1-\Delta_2)/(1+T^2)^{1/2} \ , \tag{22}$$

with

$$\Delta_1(\mathrm{CDP}) = E(\Gamma_7,\pm\tfrac{5}{2}) - E(\Gamma_6,\pm\tfrac{1}{2}) \ , \tag{23}$$

$$\Delta_2(\mathrm{CDP}) = E(\Gamma_7,\pm\tfrac{3}{2}) - E(\Gamma_6,\pm\tfrac{1}{2}) \ . \tag{24}$$

These expressions are general ones which are independent of the specific interaction model.

B. Analysis of the various approximations for Eqs. (19)–(24)

1. Cubic symmetry approximation (Refs. 5–7 and 9)

There is a ZFS of the ${}^6S$ ground state in strictly cubic symmetry, the $|\pm\frac{5}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$ states being, in general, $3a$ higher in energy than the $|\pm\frac{3}{2}\rangle$ states. In this case, we have

$$T = (5)^{1/2}/2 \ ,$$

$$\Delta_1 = 0 \ ,$$

$$a = -\Delta_2/3 = \tfrac{1}{3}[E(\Gamma_6,\pm\tfrac{1}{2}) - E(\Gamma_7,\pm\tfrac{3}{2})] \ . \tag{25}$$

2. Konig and Schnakig approximation (Ref. 2)

When $|(a+2F/3)/D| \to 0$ and $|a/D| \to 0$, we obtain

$$D \simeq \tfrac{1}{4}(\Delta_1/3+\Delta_2) \ . \tag{26}$$

C. The approximate equivalence between generalized point-charge model containing an average covalency and self-consistent-field molecular-orbital calculations

It is well known that the cubic crystal-field parameter $10Dq$ changes with metal-ligand (M-L) bond length R according to the equation

$$10Dq = CR^{-5} \ , \tag{27}$$

where C is a numerical factor which includes the position and values of the ligand point charges and the characteristics of the metal-ion wave function $R_{3d}(r)$. An experimental test of this equation is provided by the analysis of optical spectra under high pressure. Using bulk compressibility data, Minomura and Drickamer[12] have shown that the change in $\ln(Dq/Dq_0)$ with pressure coincides with the change in $-\frac{5}{3}\ln(V/V_0)$, as predicted from Eq. (1), for Al_2O_3:Ti^{3+}, Al_2O_3:V^{3+}, and Al_2O_3:Ni^{2+}. Furthermore, Drickamer used high-pressure optical measurements (up to 150 kbar) combined with P-V data to show that in NiO the R^{-5} law [Eq. (1)] is satisfied within the accuracy of the data.[13] These results were supported by subsequent works on Cr^{3+}, Fe^{2+}, Mn^{2+}, Fe^{3+}, and Co^{2+} ions in crystals.[14–20] In the framework of the Wolfberg-Helmholz semiempirical molecular-orbital (MO) theory,[21] where $10Dq$ is associated with the difference between the molecular-orbital energies $E(e_g)$ and $E(t_{2g})$, Burns and Axe[22] computed the R dependence of $10Dq$ by calculating the exponent n in the equation $10Dq=CR^{-n}$. They found a value of n close to 5 in the fluorides of Ni^{2+} and V^{2+}. Values lying between 4 and 6 have been calculated for transition-metal ions in fluorides,[23] while the analysis of experimental data for Mn^{2+}doped fluoroperovskites[24] is consistent with $n\simeq 5$. This means that the R^{-5} law is a good approximation, in view of both the MO calculations and the experiments. Now let us study the relationship between the self-consistent-field (SCF) MO model and our generalized point-charge model containing an average covalence.[3,4,14–20] It is known that the usual point-charge crystal-field model is not capable of yielding good crystal-field splittings for some clusters. However, when it is employed with a semi-SCF double-ξ d orbital as has been done by Zhao and co-workers, it can be made to agree with the observed results. This is because the semi-SCF d-orbital model contains the contributions not only of the equivalent point charges and dipoles but also of the average covalency.

In the generalized point-charge model containing an average covalency, the semi-SCF (or parametrized) double-ξ orbital is given by

$$R_d(r)=a_1[(2\xi_1)^7/6!]^{1/2}r^2\exp(-\xi_1 r/a_0)+a_2[(2\xi_2)^7/6!]^{1/2}r^2\exp(-\xi_2 r/a_0)\ , \tag{28}$$

where $a_0=$ Bohr radius $=0.52918$ Å and ξ_1,ξ_2 are the Slater exponents, with

$$a_1^2+a_2^2+2a_1a_2[2(\xi_1\xi_2)^{1/2}/(\xi_1+\xi_2)]^7=1\ . \tag{29}$$

The three approximate conditions are as follows:

(i) the overlap condition between R_d and R_d^w is given by

$$\langle R_d|d_d^w\rangle\simeq 1\ , \tag{30}$$

where R_d^w is Watson's SCF orbital;

(ii) an expectation-value condition is given by

$$\langle R_d|r^{-3}|R_d\rangle\simeq\langle R_d^w|r^{-3}|R_d^w\rangle\ ; \tag{31}$$

(iii) one parametrization condition for $\langle R_d|r^4|R_d\rangle$ yields reasonable crystal-field parameters.

Clearly, condition (iii) is an empirical one. It must be pointed out that these orbitals have been shown to be successful in interpreting not only the free-ion spectra but also the d-d crystal-field transitions, the g factors, the zero-field splitting, and the high-pressure dependence of the optical spectra in a number of crystals.[3,4,14–20] This means that the agreement between theory and experiments is not accidental and indicates that the technique may be used as a starting point for more sophisticated calculation of d^n ions in crystals. In a sense, it should be justified further by using an improving molecular-orbital calculation.

The pure electronic d-d spectrum of MnF^{4-} in vacuo and in $RbMnF_3$ has been computed at different values of the Mn^{2+}-F^- bond length R, following an open-shell SCF MO methodology.[23,25] This is an important development.

Following the generalized point-charge model containing an average covalency,[3,4,14–20] the semi-SCF orbital of the Mn^{2+} ion is given by[20]

$$R_d(r)=0.639\,22[10^7/6!]^{1/2}r^2\exp(-5r/a_0)+0.600\,00[3^7/6!]^{1/2}r^2\exp(-1.5r/a_0)\ . \tag{32}$$

Using a computer, we find

$$\langle r^2\rangle_0=2.7755\ \text{a.u.}\ ,$$
$$\langle r^4\rangle_0=23.2594\ \text{a.u.}\ ,$$
$$\langle r^{-3}\rangle_0=4.015\,57\ \text{a.u.}\ ,$$

$$\begin{aligned}
&\xi_d^0=336.6\ \text{cm}^{-1}\\
&\qquad(\text{observed, }347\ \text{cm}^{-1};\ \text{SCF, }333\ \text{cm}^{-1})\ ,\\
&10Dq_0=5e^2\langle r^4\rangle_0/3R^5=9794\ \text{cm}^{-1}\ (R=2.117\ \text{Å})\\
&\qquad[\text{SCF, }10\,020\ \text{cm}^{-1}\ (\text{Ref. }25)]\ ,
\end{aligned}\tag{33}$$

$$A_0=154\,167\ \text{cm}^{-1}\ ,$$
$$B_0=911\ \text{cm}^{-1}\ (\text{observed, }915\ \text{cm}^{-1})\ [\text{SCF},885\ \text{cm}^{-1}\ (\text{Ref. }23)]\ ,$$
$$C_0=3273\ \text{cm}^{-1}\ (\text{observed, }3273\ \text{cm}^{-1})\ [\text{SCF},3059\ \text{cm}^{-1}\ (\text{Ref. }23)]\ ,$$
$$P=g_3g_n\beta_e\beta_n\langle r^{-3}\rangle_0=0.0187\ \text{cm}^{-1}\ (\text{SCF, }0.0187\ \text{cm}^{-1})\ .$$

The usual crystal-field parameters B_{kq} can be calculated from the local structure data provided the expectation values $\langle r^n\rangle$ and the effective charge q in the crystals are known. In general, values of $\langle r^n\rangle$ in crystals are smaller in magnitude than the free-ion values $\langle r^n\rangle_0$ as are the Racah parameters B and C, the Trees parameter α, the Racah seniority correction β, and the spin-orbit coupling constant ξ_d in crystals. This arises mainly because of covalency effects involving the overlap between the central metal ion and the ligand orbits, which reduce the free-ion values. A reasonable approximation is made that[14–20]

$$\begin{aligned}
&B=N^4B_0\ ,\ C=N^4C_0\ ,\ \alpha=N^4\alpha_0\ ,\ \beta=N^4\beta_0\ ,\\
&\xi_d=N^2\xi_d^0\ ,\ \langle r^n\rangle=N^2\langle r^n\rangle_0\ .
\end{aligned}\tag{34}$$

N measures the average reduction factor due to covalency, which is to be determined from a d-d transition band. $\alpha_0=65$ cm^{-1} and $\beta_0=-131$ cm^{-1}. A value of $N=0.984\,96$ was derived from the SCF MO d-d transition bands,[25] which leads to $B=857.41$ cm^{-1}, $C=3080.48$ cm^{-1}, $\xi_d=323.5$ cm^{-1}, $\alpha=61.18$ cm^{-1}, $\beta=-123.3$ cm^{-1}, and $Dq=\frac{1}{6}N^2e^2\langle r^4\rangle_0/R^5=805.4$ cm^{-1} ($R=2.117$ Å). The comparison between the SCF MO model and the generalized point-charge model is shown in Table I.

TABLE I. The comparison between SCF MO and generalized point-charge calculations (all numbers in cm^{-1}).

	SCF MO ($R=2.117$ Å) (Ref. 25)	Generalized point charge ($R=2.117$ Å)
$^4T_{1g}^a$	17 280	18 686
$^4T_{2g}^a$	22 380	23 030
$^4E(G)^a$	25 750	25 200
$^4A_1(G)^a$	25 710	
$^4T_{2g}^b$	28 780	28 550
$^4E_g^b$	31 000	30 345
$^4T_{1g}^b$	34 800	32 968
$^4A_{2g}$	41 980	40 914
$^4T_{1g}^c$	43 400	41 901
$^4T_{2g}^c$	47 520	44 879

It can be seen from Table I that the generalized point-charge model containing an average covalence is approximately equivalent to the SCF MO model rather than to a true electrostatic point-charge one, under the $Dq \propto R^{-5}$ law.[22–25] This is an important improvement.

D. Applications of the formulas to the optical spectra and ZFS in RbCdF$_3$:Mn^{2+}, RbMnF$_3$, and Rb$_2$CdF$_4$:Mn^{2+}

The Mn^{2+} ions in fluoroperovskites provide good examples for examining the microscopic origin of the SH theory of the $3d^5$ ions in crystals. As an illustration, formulas (17)–(24) will be applied to the specific examples of RbCdF$_3$:Mn^{2+}, RbMnF$_3$, and Rb$_2$CdF$_4$:Mn^{2+}. In Sec. II C we have given values of the electrostatic parameters B and C, the spin-orbit coupling constant ξ_d, the Racah parameter β, and the Trees parameter α. Further, the expectation values $\langle r^2\rangle$ and $\langle r^4\rangle$ of the Mn^{2+} ions in fluoroperovskites are

$$\langle r^2\rangle = N^2\langle r^2\rangle_0 = 2.692\,64 \text{ a.u.} , \qquad \langle r^4\rangle = N^2\langle r^4\rangle_0 = 22.5650 \text{ a.u.} \tag{35}$$

First, let us study RbCdF$_3$:Mn^{2+}. The Mn^{2+}-F$^-$ bond length R in cubic RbCdF$_3$:Mn^{2+} is (2.146 ± 0.012) Å by the superhyperfine splitting (HFS) method.[26] We have fitted our approximately equivalent SCF MO model to the experimental spectra[27,28] and find $R(\mathrm{Mn}^{2+}\text{-}\mathrm{F}^-) = (2.1474\pm0.0005)$ Å ($Dq = \frac{1}{6}[N^2e^2\langle r^4\rangle_0/R^5] = 750$ cm^{-1}) which is comparable to the value of $R=(2.146\pm0.012)$ Å by the HFS method,[26] which supports the determination of the bond length through the optical spectrum and the EPR spectrum on the basis of an approximately equivalent SCF MO model. The comparison between the observed and the calculated spectra is shown in Table II. It can be seen from Table II that the calcu-

TABLE II. Calculated and observed spectra for RbMnF$_3$ and RbCdF$_3$:Mn^{2+} (all numbers in cm^{-1}).

Calc. ($R=2.1474$ Å)		Obs. (Refs. 27 and 28) (300 K)		Calc. ($R=2.1395$ Å)		Obs. (Ref. 27) (77 K)
O_h	O_h'	RbMnF$_3$	RbCdF$_3$	O_h	O_h'	RbMnF$_3$
19 212	19 143	19 286	19 530±40	19 080	19 010	19 151
($^4T_1^a$)	19 167				10 035	
	19 228			($^4T_1^a$)	19 097	
	19 274				19 143	
23 343	23 235	23 120	23 670±50	23 266	23 159	23 106
($^4T_2^a$)	23 285			($^4T_2^a$)	23 208	
	23 395				23 318	
	23 400	23 282			23 324	
25 200	25 186	25 202	25 230±20	25 200	25 186	25 208
[$^4A_1^a(G)$,	25 190	25 335		[$^4A_1^a(G)$,	25 189	25 341
$^4E^a(G)$]	25 204			$^4E^a(G)$]	25 204	
	25 205				25 205	
26 179	25 280	25 500		25 924	25 568	25 575
$^2\Gamma$ (doublet)	26 414	25 610		($^2\Gamma$)	26 162	25 959
28 670	28 505	28 110	28 350±70	28 639	28 475	27 917
[$^4T_2^b$]	28 524	28 385		[$^4T_2^b$]	28 493	28 385
	28 768				28 737	
	28 879				28 846	
30 345	30 308	30 067	30 070±50	30 345	30 310	30 140
[$^4E^b$]	30 326	30 393		[$^4E^b$]	30 326	30 478
	30 348				30 348	
32 590	32 520	32 414	32 270±140	32 686	32 625	32 446
[$^4T_1^b$]	32 535	32 630		[$^4T_1^b$]	32 705	32 789

TABLE II. (*Continued*).

Calc. ($R = 2.1474$ Å)		Obs. (Refs. 27 and 28) (300 K)		Calc. ($R = 2.1395$ Å)		Obs. (Ref. 27) (77 K)
O_h	O_h'	$RbMnF_3$	$RbCdF_3$	O_h	O_h'	$RbMnF_3$
	32 624				32 746	
	32 688				32 785	
4 0914	41 183	41 152		40 914	41 169	41 158
$[{}^4A_2]$				$[{}^4A_2]$		
41 753	41 551	41 920		41 790	41 581	41 920
$[{}^4T_1^c]$	41 691			$[{}^4T_1^c]$	41 724	
	41 852				41 888	
	41 864				41 899	
44 447	44 326	43 914		44 554	44 431	44 200
$[{}^4T_2^c]$	44 370			$[{}^4T_2^c]$	44 474	
	44 412				44 494	
	44 571				44 666	
				Double excitation (Ref. 25)		
				38 160	38 020	38 300
				$({}^4T_1^a+{}^4T_1^a)$	38 070	
					38 194	
					38 286	
				42 346	42 169	42 200
				$({}^4T_1^a+{}^4T_2^a)$	42 243	
					42 415	
					42 467	
				44 280	44 196	43 900
				$({}^4T_1^a+{}^4A_1^a,{}^4E^a)$	44 224	
					44 301	
					44 348	
				46 532	46 318	46 700
				$({}^4T_2^a+{}^4T_2^a)$	46 416	
					46 636	
					46 648	
				47 719	47 485	47 300
				$({}^4T_1^a+{}^4T_2^b)$	47 528	47 800
					47 834	
					47 989	
				48 466	48 345	48 400
				$({}^4T_2^a+{}^4A_1^a,{}^4E^a)$	48 397	48 900
					48 522	
					48 529	
				49 425	49 320	49 200
				$({}^4T_1^a+{}^4E^b)$	49 491	
				50 400	50 372	50 800
				$({}^4A_1^a,{}^4E^a+{}^4A_1^a,{}^4E^a)$	50 378	
					50 408	
					50 410	
EPR parameter		$(9\pm2)\times10^{-4}$				
a		(Ref. 31)				
5.49×10^{-4}		$(4.7\pm0.2)\times10^{-4}$				
		(Refs. 32 and 33)				

TABLE III. ZFS parameters of Rb_2CdF_4:Mn^{2+}.

	D (10^{-4} cm^{-1})	
Calc.	CDP	Konig and Schnakig approx.
	60 ± 0.05	55
Obs. (Ref. 30)	60 ± 0.7	
	$a+2F/3$ (10^{-4} cm^{-1})	
Calc.	CDP	Konig and Schnakig approx.
	5.76 ± 0.03	~0
Obs. (Ref. 30)	5.6 ± 0.4	
	a (10^{-4} cm^{-1})	
Calc.	CDP	Konig and Schnakig approx.
	6.14 ± 0.03	~0
Obs. (Ref. 30)	6.1 ± 0.9	

lated results are in good agreement with experiment.

In addition, by means of this procedure, it is predicted that $\alpha=(dR/dT)/R=(16.5\pm0.4)\times10^{-6}$ K^{-1} [$R=(2.1474\pm0.0005)$ Å at 300 K and (2.1395 ± 0.0005) Å at 77 K], which is in good agreement with the experimental thermal expansion coefficient $(16.5\pm0.5)\times10^{-6}$ K^{-1} for $RbMnF_3$.[26,29]

For tetragonal symmetry, the crystal-field parameters are given by

$$B_{20}=-2e^2\langle r^2\rangle(1/R_1^5-1/R_2^5)\ , \tag{36}$$

$$B_{40}=e^2\langle r^4\rangle(3/R_1^5+4/R_2^5)/2\ , \tag{37}$$

$$B_{44}=(\tfrac{35}{2})^{1/2}e^2\langle r^4\rangle(1/R_1^5)/2\ , \tag{38}$$

where R_2 stands for the bond length of Mn^{2+}-F^- along the chosen Z axis, R_1 is the bond length of Mn^{2+}-F^- in the plane which is perpendicular to the Z axis, e is the electronic charge, and $\langle r^n\rangle$ ($n=2,4$) the expectation value of the radial coordinate of an electron.

Using Eqs. (35)–(38) and Eqs. (17)–(24), we have fitted our ZFS expressions to the experimental ZFS parameters D and a,[30] and find $R_2=(2.1446\pm0.0002)$ Å and $R_1=(2.13\pm0.0002)$ Å, which are comparable to the values of $R_2=(2.146\pm0.015)$ Å and $R_1=(2.06\pm0.012)$ Å of K_2MgF_4:Mn^{2+} obtained by the HFS method.[26] The result is shown in Table III. It is interesting to note that the predicted value of $a+2F/3=(5.76\pm0.03)\times10^{-4}$ cm^{-1} is in good agreement with the experimental value of $(5.6\pm0.04)\times10^{-4}$ cm^{-1} (Ref. 29). In addition, the predicted d-d transition bands shown in Table IV can be verified by further absorption experiments.

E. Discussion and conclusion of Sec. II

(a) We have studied in detail the analytical expressions for the ZFS of $3d^5$ ions in tetragonal symmetry. The main results are (i) a(calc)$=5.49\times10^{-4}$ cm^{-1} [$(4.7\pm0.2)\times10^{-4}$ cm^{-1} (Refs. 32 and 33); $(9\pm2)\times10^{-4}$ cm^{-1} (Ref. 31)] for Mn^{2+} in $RbCdF_3$, and (ii) D(calc)$=(60\pm0.05)\times10^{-4}$ cm^{-1} [$(60.2\pm0.7)\times10^{-4}$ cm^{-1} (Ref. 30)], $(a+2F/3)$(calc)$=(5.76\pm0.03)\times10^{-4}$ cm^{-1} [$(5.6\pm0.4)\times10^{-4}$ cm^{-1} (Ref. 30)] and a(calc)$=(6.14\pm0.3)\times10^{-4}$ cm^{-1} [$(6.1\pm0.9)\times10^{-4}$ cm^{-1} (Ref. 30)] for Mn^{2+} in Rb_2CdF_4 which reveal that

TABLE IV. The predicted $^6\Gamma\rightarrow{}^4\Gamma$ d-d transition bands (all numbers in units of cm^{-1}).

O_h	D'_{4h}
19 215	18 884
($^4T_1^a$)	18 896
	18 993
	19 029
	19 046
	19 080
23 345	23 080
($^4T_2^a$)	23 116
	23 156
	23 255
	23 332
	23 348
25 200	25 185
[$^4A_1^a(G)$,$^4E^a(G)$]	25 186
	25 187
	25 202
	25 205
	25 206
28 675	28 434
($^4T_2^b$)	28 473
	28 475
	28 703
	28 739
	28 829
30 345	30 308
($^4E^b$)	30 323
	30 326
	30 346
32 593	32 640
($^4T_1^b$)	32 688
	32 725
	32 775
	32 840
	32 853
40 914	40 432
($^4A_2$)	40 889
41 755	41 598
($^4T_1^c$)	41 737
	41 750
	41 899
	41 920
	41 922

both the approximately equivalent SCF MO model and the ZFS expressions provide a reasonable interpretation of the microscopic origin of the ZFS of $3d^5$ ions in cubic and tetragonal symmetries. In view of the excellent agreement between theory and experiments achieved in this study, both the model and ZFS expressions are reasonable.

(b) Earlier works[2] calculated the rank-2 parameter D or E only, with some approximations, due to the complexity of the problem, without consideration of the rank-4 ZFS parameters F and a. The analytical expressions used here show that the earlier approximate formula[2] for D is a good one when $|(a+2F/3)/D|<0.1$ and $|a/D|<0.1$. However, it is incorrect when $|(a+2F/3)/D|\sim 1$ and $|a/D|\sim 1$.

(c) The effective spin-Hamiltonian formalism for $3d^5$ in D'_{4h} is a good approximation within the framework of the microscopic CDP.

(d) The deduced Mn^{2+}-F^- bond length of $R=(2.1474\pm 0.0005)$ Å at 300 K is comparable to the value of $R=(2.146\pm 0.012)$ Å for $RbCdF_3:Mn^{2+}$ obtained by the HFS method. Furthermore, the predicted thermal expansion coefficient and EPR cubic parameter $a=5.49\times 10^{-4}\ \mathrm{cm}^{-1}$ are in good agreement with experiments, which supports the determination of the bond length through the optical spectrum and EPR spectrum on the basis of an approximately equivalent SCF MO model.

III. C'_3 SYMMETRY

A. Analytical expressions for ZFS parameters in C_{3v} symmetry

The irreducible representations of the double group C'_3 arising from the $3d^5$ configuration are Γ_4, Γ_5^* and $\Gamma_6, \Gamma_5^*=\Gamma_4$, which yield 84×84 matrices which are functions of the electrostatic parameters B and C, the Trees and Racah parameters α and β, the spin-orbit constant ξ_d, and the crystal-field parameters B_{20}, B_{40}, B_{43}, and B_{4-3}.[17,34,35] The irreducible representations and 84×84 matrix are deposited in the AIP's Physics Auxiliary Publication Service.[8]

In order to analyze the EPR spectrum, the spin Hamiltonian for the axially symmetry case about a threefold axis was used. This is given by[11]

$$H_s=\beta(g_{\parallel}S_zH_z+g_{\perp}S_xH_x+g_{\perp}S_yH_y)+B_2^0O_2^0+B_4^0O_4^0+B_4^3O_4^3 \ . \tag{39}$$

The symbols appearing in Eq. (39) have their usual meanings.

The coordinate system is chosen such that the Z axis coincides with the symmetric axis C_3. The spin-Hamiltonian matrix elements are calculated in terms of the effective spin vectors. The spin ground state of the $3d^5$ configuration in a crystal is an admixture of $S=\frac{5}{2},\frac{3}{2}$, and $\frac{1}{2}$ spin states. In the effective spin-Hamiltonian formalism,[7,9,10] the "spin" is described by an effective spin S'. In the case of high spin, $S'=\frac{5}{2}$, in $3d^5$ ions in a crystal field. This is a good approximation.

By means of the approximate equivalence between the SH and CDP, the following ZFS expressions are obtained:

$$D=[9\Delta_1/(1+T^2)^{1/2}+\Delta_1-2\Delta_2]/56 \ , \tag{40}$$

$$a-F=[3\Delta_1/(1+T^2)^{1/2}+18\Delta_2-9\Delta_1]/28 \ , \tag{41}$$

$$a=3\Delta_1 T/[80(1+T^2)]^{1/2} \ , \tag{42}$$

with

$$T=-2a_1a_2/(a_1^2-a_2^2) \ , \tag{43}$$

$$\Delta_1=E(\Gamma_4,-\tfrac{5}{2})-E(\Gamma_4,\tfrac{1}{2}) \ , \tag{44}$$

$$\Delta_2=E(\Gamma_{6,}\tfrac{3}{2})-E(\Gamma_4,\tfrac{1}{2}) \ , \tag{45}$$

$$D=3B_2^0 \ , \tag{46}$$

$$a-F=-180B_4^0 \ , \tag{47}$$

$$a=(9/\sqrt{2})B_4^3 \ , \tag{48}$$

where $E(\Gamma_4,-\frac{5}{2})$ and $E(\Gamma_4,\frac{1}{2})$ denote the eigenenergies of the Γ_4 CDP ground sites for $|-\frac{5}{2}\rangle$ and $|\frac{1}{2}\rangle$, respectively. $E(\Gamma_6,\frac{3}{2})$ is the eigenenergy of the Γ_6 CDP ground state for $|\frac{3}{2}\rangle$. a_1 and a_2 denote the CDP eigenvector of the ground state of Γ_4:

$$|\tfrac{1}{2}\rangle(\mathrm{CDP})=a_1|{}^6S,\tfrac{1}{2}\rangle+a_2|{}^6S,-\tfrac{5}{2}\rangle+\text{small contributions arising from the } S=\tfrac{3}{2} \text{ and } S=\tfrac{1}{2} \text{ states} \ . \tag{49}$$

These expressions are general ones which are independent of the specific interaction model.

B. Analysis of the various approximations for Eqs. (40)–(45)

1. ZFS in a cubic field (Refs. 6 and 7)

There is a ZFS of the $3d^5$ ground state in strictly cubic symmetry, the $|\pm\frac{3}{2}\rangle$ state being, in general, $3a$ higher in energy than the $|\pm\frac{1}{2}\rangle$ state. In this case we have

$$T=\sqrt{80} \ , \tag{50}$$

$$D=F=0 \ , \tag{51}$$

$$a=\Delta_1/3 \ . \tag{52}$$

This is the conventional cubic approximation. Calculations indicate that the ZFS is highly dependent on Dq, ξ_d, B, and C.

2. Small-$(a-F)$ approximation (Ref. 17)

When $|a/D|\ll 1$ and $|(a-F)/D|\ll 1$, we obtain

$$D\simeq(5\Delta_1-\Delta_2)/28 \ , \tag{53}$$

TABLE V. Comparison between accurate and approximate formulas ($B=823.26\ \mathrm{cm}^{-1}$, $C=2957.77\ \mathrm{cm}^{-1}$, $\alpha=58.74\ \mathrm{cm}^{-1}$, $\beta=-118.38\ \mathrm{cm}^{-1}$, $\xi_d=320\ \mathrm{cm}^{-1}$).

B_{20} (cm^{-1}) B_{40} (cm^{-1}) B_{43} (cm^{-1})	D (10^{-4} cm^{-1})		$a-F$ (10^{-4} cm^{-1})		a (10^{-4} cm^{-1})	
	CDP	Febbraro's approx.	CDP	Febbraro's approx.	CDP	Febbraro's approx.
−942.34 −17 241.15 27 598.93	2407.9	2547.3	166.5	$\simeq 0$	94.4	$\simeq 0$
−536.25 −18 381.11 25 604.93	1120.5	1203.9	99	$\simeq 0$	74.1	$\simeq 0$
−470.42 −18 513.31 25 266.03	948.5	1025.4	91	$\simeq 0$	70.9	$\simeq 0$
−435.837 −19 563.125 23 568	39.4	103.3	59.6	$\simeq 0$	60.3	$\simeq 0$

$$a-F\simeq\tfrac{3}{14}(3\Delta_2-\Delta_1)\ . \qquad (54)$$

This is a good approximation.

3. *Febbraro's approximation (Refs. 34 and 35)*

When $|a/D|\sim 0$ and $|(a-F)/D|\sim 0$, we obtain

$$D\simeq\Delta_2/2\ . \qquad (55)$$

Calculations show that, in general, this approximation is a good one when $|a/D|<0.1$ and $|(a-F)/D|<0.1$ as shown by Table V. However, it is incorrect when $|a/D|\sim 1$ and $(a-F)/D|\sim 1$.

C. Calculation and results

In the generalized crystal-field model by Zhao *et al.*[14–20], the C_{3v} (D_{3d}) crystal-field parameters B_{kq} and the electrostatic parameters are as follows:

$$B_{20}=[-eq\langle r^2\rangle/2]\sum_{i=1}^{6}(3\cos^2\theta_i-1)/R_i^3\ , \qquad (56)$$

$$B_{40}=[-eq\langle r^4\rangle/8]\sum_{i=1}^{6}(35\cos^4\theta_i-30\cos^2\theta_i+3)/R_i^5\ , \qquad (57)$$

$$B_{43}=-B_{4-3}=[3\sqrt{35}eq\langle r^4\rangle/12]\times\sum_{i=1}^{6}(\cos\theta_i\sin^3\theta_i)/R_i^5\ , \qquad (58)$$

$$B=N^4B_0\ ,\quad C=N^4C_0\ ,\quad \alpha=N^4\alpha_0\ ,\quad \beta=N^4\beta_0\ ,$$
$$\xi_d=N^2\xi_d^0\ ,\quad \langle r^k\rangle=N^2\langle r^k\rangle_0\ . \qquad (59)$$

For the Fe^{3+} ion, we have[17]

$$B_0=1130.22\ \mathrm{cm}^{-1}\ (\mathrm{SCF},\ 1100\ \mathrm{cm}^{-1}),$$
$$C_0=4111.45\ \mathrm{cm}^{-1}\ (\mathrm{SCF},\ 4000\ \mathrm{cm}^{-1}),$$
$$\xi_d^0=588.946\ \mathrm{cm}^{-1}\ (\mathrm{SCF},\ 575\ \mathrm{cm}^{-1}),$$
$$\langle r^2\rangle_0=1.890\,39\ \mathrm{a.u.},$$
$$\langle r^4\rangle_0=11.464\,85\ \mathrm{a.u.},$$
$$\alpha_0=40\ \mathrm{cm}^{-1}\ ,\quad \beta_0=-131\ \mathrm{cm}^{-1}\ , \qquad (60)$$

which are in good agreement with the optical bands of the free ions.[17]

As an illustration, the formulas (40)–(49) and (56)–(60) will be applied to the specific example of α-Al_2O_3:Fe^{3+}. For Fe^{3+}-doped corundum, we have found $N=0.864$ from the optical absorption spectra in α-Al_2O_3:Fe^{3+} crystals. In the calculation, $q=$ valence charge $=-2e$. The good agreement between theory and experiments shows that $q=-2e$ is a reasonable value for the Fe^{3+} ion.[3] It will be used in our calculations.

Using $N=0.864$ and diagonalizing the Γ_4 matrix (84×84), and Γ_6 matrix (84×84) in the C_3' double group, and then substituting the values of Δ_1, Δ_2, a_1, and a_2 deduced into the analytical expressions for D, $a-F$, and a, we obtained the results shown in Tables VI and VII. It can be seen that the theoretical values are in good agreement with the experimental data. Apparently, the models that have a correct and clear physics meaning will be those which agree well with experimental results. It is noted that, in the calculation of D, a, and F presented, the parameters N and q used were obtained from independent optical measurements, without introduction of any adjustable parameter. Therefore it is safe to say that these models are reasonable.

TABLE VI. Calculated and observed *d*-*d* transition for α-Al_2O_3:Fe^{3+} (all values are in units of cm^{-1}). For the α-Al_2O_3 single crystal, to within the range of experimental error, the structure data are $R_1=R_2=R_3=1.857$ Å, $R_4=R_5=R_6=1.966$ Å, $\theta_1=\theta_2=\theta_3=62.7°$, $\theta_4=\theta_5=\theta_6=46.7°$ (Refs. 36 and 37).

		CDP	
O_h	C_{3v}	C'_{3v}	Observed (Ref. 40)
$^4T_1(G)$	10 070	9 790	9450–9700
	100 445	10 048	
		10 229	
		10 392	
		10 473	
		10 493	
$^4T_2(G)$	14 203	14 229	14 350
	14 330	14 262	
		14 315	
		14 373	
		14 399	
		14 401	
$^4A_1(G)$	18 200	17 977	17 600–17 800
$^4E(G)$	18 188	17 998	
		18 101	
		18 143	
		18 188	
		18 199	
$^4T_2(D)$	20 294	20 181	
	20 455	20 191	
		20 341	
		20 533	
		20 562	
		20 823	
$^4E(D)$	22 283	22 299	22 120–22 200
		22 313	
		22 319	
		22 328	
$^4T_1(P)$	25 862	25 652	25 680–26 700
	26 468	25 805	
		25 945	
		26 141	
		26 330	
		26 457	
$^4A_2$	30 015	30 167	29 000
		30 170	

D. Discussion and conclusion of Sec. III

(a) In the spin-Hamiltonian formalism for the trigonal symmetry, we have[9]

$$\Delta_1(\mathrm{SH})=\tfrac{1}{3}[(a-F+18D)^2+80a^2]^{1/2}\ , \tag{61}$$

$$\Delta_2(\mathrm{SH})=\tfrac{3}{2}(a-F)-D+\tfrac{1}{6}[(a-F+18D)^2+80a^2]^{1/2}\ . \tag{62}$$

To gain insight into the equivalence between the SH and our CDP Eqs. (40)–(49), we substitute the calculated values of the ZFS parameters of Table V into Eqs. (61) and (62), and obtain the result shown by Table VIII. It can be seen that the CDP values are in excellent agreement with the SH ones. It follows from this that our CDP Eq. (40)–(49) are accurate ones within the framework of crystal-field theory. In other words, the spin-Hamiltonian formalism is a very good equivalent approximation for the ZFS of $3d^5$ ion in a C_3 symmetry crystal field.

(b) The analytical expressions reported here for the EPR parameters D, $a-F$, and a in a trigonal crystal field within the framework of the CDP are general formulas, independent of the specific interaction model. They are also valid when spin-spin and other interactions are involved in Eq. (1).

(c) Earlier works[34,35] calculated the rank-2 parameter D only, without consideration of rank-4 ZFS parameters a and F, because of the complexity of the problem. The present accurate scheme shows that Febbraro's approximation is a good one when $|a/D|<0.1$ and $|(a-F)/D|<0.1$. However, it is incorrect when $|a/D|\sim 1$ and $|(a-F)/D|\sim 1$.

(d) For α-Al_2O_3:Fe^{3+}, taking $B_{20}=0$ and $B'_{40}=0$, we find that $D=0$, $F=0$, $a(\mathrm{cubic})=225\times10^{-4}$ cm^{-1}, and $a(\mathrm{trigonal})-a(\mathrm{cubic})=29\times10^{-4}$ cm^{-1}, which indicate that the trigonal crystal-field components have a remarkable contribution to the rank-4 parameter a.

(e) The generalized crystal-field model and the analytical expressions (40)–(49) can simultaneously account for the optical bands and EPR parameters D, $a-F$, and a for the α-Al_2O_3:Fe^{3+} crystal. In the calculation for D, a, and F, the parameters N and q used were obtained from

TABLE VII. Calculated and observed ZFS for α-Al_2O_3:Fe^{3+} (all values are in units of 10^{-4} cm^{-1}).

D (calc)		D (obs) (Refs. 38 and 39)
CDP formulas[a]	Febbraro approx.	
1784	2063	1718±2, 1682±2
$(a-F)$ (calc)		$(a-F)$ (obs) (Refs. 38 and 39)
CDP formulas	Febbraro approx .	
322	$\simeq 0$	329±2, 333±2
a (calc)		a (obs) (Refs. 38 and 39)
CDP formulas	Febbraro approx.	
254	$\simeq 0$	241±4, 262±20

[a] D(spin-spin)$=-6$, D(spin-spin-SO)$=2$, D(Orbach-Das-Sharma)$\simeq 0$ (see Ref. 3).

TABLE VIII. Comparison between SH and CDP (all values are in units of 10^{-4} cm^{-1}).

D (CDP)	$a-F$ (CDP)	a (CDP)	Δ_1 (SH)	Δ_1 (CDP)	Δ_2 (SH)	Δ_2 (CDP)
39.4	59.6	60.3	313.039	313.183	206.520	206.645
948.5	91	70.9	5 725.237	5 725.355	2 050.610	2 050.727
1120.5	99	74.1	6 759.611	6 759.442	2 407.805	2 407.750
2407.9	166.5	94.4	14 505.630	14 505.510	5 094.665	5 094.600

independent optical measurement, without introduction of any adjustable parameter. Therefore it is safe to say that these models and results are reasonable. Of course, our calculated values must be justified by further measurements.

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[8] See AIP document No. PAPS PRBMDO-52-10043-68 for 68 pages of irreducible basis functions and the Hamiltonian matrix of $3d^5$ ions in low-symmetry fields. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, Carolyn Gehlbach, 500 Sunnyside Boulevard, Woodbury, New York, 11797. Fax: 516-576-2223, e-mail: janis@aip.org. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.

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