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Comprehensive approach to the zero-field splitting of ^6S-state ions: Mn^{2+} and Fe^{3+} in fluoroperovskites

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The zero-field splitting of ^6S-state ions is studied in the intermediate-field coupling scheme by taking the crystal-field and the electrostatic interactions as the unperturbed Hamiltonian and the spin-orbit interaction as a perturbation. This perturbation process shows a very good convergence and provides a comprehensive approach to the derivation of both the rank-2 b_2^q and the rank-4 b_4^q zero-field splitting parameters, which are shown to come predominantly from the first nonzero perturbation terms. Cubic and tetragonal symmetries are considered and the zero-field splitting parameters D ($\sim b_2^0$), a ($\sim b_4^4$), and F ($\sim b_4^0$) are investigated in detail as functions of the cubic Dq and the tetragonal crystal-field (CF) parameters B_{20} and B'_{40}. It is found that the tetragonal CF components B_{20} and B'_{40} contribute, to the cubic zero-field splitting parameter a, a value a_t, which is non-negligible. The ratio a_t/F is found to be insensitive to CF parameters and to lie in the range -0.2 to -0.5. Both parameters a_t and F depend mainly on B_{20}, whereas D depends mainly on B'_{40}. The results of earlier perturbation procedures are also calculated and compared with the present ones. The present theory deals with the zero-field splitting parameters b_k^q ($k=2$ and 4) by regarding the crystal-field parameters B_{kq} ($k=2$ and 4) as freely adjustable phenomenological parameters, thus avoiding problems arising from the application of a specific crystal-field model to the evaluation of B_{kq}. Following this idea, numerical calculations are carried out for the parameters a, D, and F for Mn^{2+} and Fe^{3+} ions in cubic and tetragonal fluoroperovskites. The results are in good agreement with experimental data. This work presents examples where the crystal-field theory allows a successful interpretation of the zero-field splitting of ^6S-state ions.

I. INTRODUCTION

The microscopic theory of the spin Hamiltonian (SH) of ^6S-state ions has received a great amount of interest in recent years (see, e.g., Refs. 1–3). Since the orbital angular momentum of the ground state is zero, it is necessary to take into account higher-lying multiplets, which involves tedious calculations. It has been established that the combined effect of the spin-orbit and crystal-field (CF) interactions accounts for the experimentally observed zero-field splitting (ZFS) of ^6S-state ions in many ionic crystals.[2–16] On the other hand, the role of other effects, in particular overlap[17–20] and relativistic CF (Refs. 21–23) effects, has been indicated. However, to date there has been no work in the literature that takes into account all of the mechanisms and that yields good agreement between calculated and experimental results.

The ZFS parameters for symmetries lower than cubic cannot be calculated by diagonalizing the full energy matrices within the whole d^5 configuration, including the CF and spin-orbit potentials, to give "accurate" values contributed by these two interactions, since there are three or more independent ZFS parameters, but only three Kramers energy levels in the ground ^6S state. Assumptions have to be made when deducing the ZFS parameters from the energy splittings of ^6S state obtained by diagonalization in order to produce an approximate result. A commonly used approximation is to omit in the spin Hamiltonian calculations rank-4 ZFS terms and to consider only the rank-2 axial term D (or b_2^0) for tetragonal (first kind; see Ref. 24) and trigonal symmetries. A plausible justification is that the former terms are much smaller in magnitude than the rank-2 terms for crystals strongly distorted from cubic.[11–14] It seems, however, that there are no similar assumptions and approximations allowing a calculation of the rank-4 ZFS parameters.

Perturbation calculations have been useful in the study of the ZFS of ^6S-state ions.[2–10,6–23,25–27] Three alternative perturbation procedures have been suggested for the calculation of the rank-2 ZFS parameters of ^6S-state ions (see, e.g., Ref. 3). In addition to the well-known procedure proposed by Blume and Orbach (BO),[25,26] the one proposed by Watanabe[27] has been extended and extensively adopted recently.[3–7] The perturbation procedure suggested by Macfarlane[28] and Zdansky[29] (MZ) for $^4A_2(d^3/d^7)$ and $^3A_2(d^2/d^8)$ ions has been also applied to the ^6S-state ions.[3,8,9] All the three procedures regard the spin-orbit coupling and low-symmetry CF component as a perturbation term. In addition, the perturbation Hamiltonian also includes the cubic CF part in the Watanabe procedure and off-diagonal part of the electrostatic interaction in the MZ procedure (see, e.g., Ref. 3).

Cubic,[8,16] tetragonal,[3,4,9,13] trigonal,[3,7] orthorhombic,[3,6] and even monoclinic[5] symmetries have been dealt with. Most of these works,[3–7,10–14,17–21,23] however, are limited to the lowest orders of perturbation, and that casts doubt on the convergency of the perturbation procedure (see, e.g., Ref. 30). Checking the convergency of the proposed perturbation procedures requires extensive calculations.

Most of the earlier works were limited to rank-2 ZFS parameters such as D and E, since they are much easier to deal with than the rank-4 terms. Recently, the significance of including the rank-4 ZFS parameters in the study of the microscopic SH theory of ^6S-state ions has been pointed out.[9] The rank-4 ZFS parameters themselves, in particular the cubic parameter a, play an important role in ^6S-state splitting and are interrelated with the rank-2 ZFS parameters. However, the calculation of the rank-4 ZFS parameters is much more complicated since they arise from fourth- and higher-order effects of spin-orbit and CF interactions. An analytical formula for the cubic ZFS parameter a and a subsequent semiempirical expression for a have been derived.[8] This enables one to explain the observed static and stressed electron paramagnetic resonance (EPR) data for Fe^{3+} and Mn^{2+} ions in several octahedral crystals.[8] A perturbation calculation recently has been carried out for tetragonal symmetry[9] using the MZ technique.[28,29] Separating the cubic ZFS term a into two parts, i.e., a_c arising from a cubic CF and a_t (denoted as a' in Ref. 9) due to the tetragonal CF components, Yu[9] has found that a_t is related closely to the rank-4 axial term F by the ratio $a_t/F \cong -\frac{1}{2}$. The validity of this relationship needs further confirmation because the calculations[9] have been made only in the lowest-order perturbation.

Considering the combined effect of the CF and spin-orbit interactions within the d^5 configuration as the origin of the ZFS of ^6S-state ions, we obtain that each of the ZFS parameters b_k^q is related with all of the CF parameters B_{kq}. The experimental values of the latter parameters for $3d^5$ ions are rather scarce. In past works, in which only rank-2 ZFS terms were considered, one has resorted to various CF models which relate CF parameters B_{kq} and the crystallographic parameters to get an idea of the values of B_{kq}. Additional problems thus arise, namely, the intrinsic problems inherent in a given CF model itself (e.g., assumptions, approximations, etc.), as well as doubts as to the accuracy of the crystallographic data used, which reduce the reliability of the final ZFS results even further. Moreover, usually the changes in the local host structure due to dilute impurities doped in the crystal are neglected. We need to separate the microscopic SH theory from these problems in order to avoid the difficulties induced by the application of specific CF models. As matter of fact, there has been no CF model which could reasonably well explain the optical spectra of $3d^N$ ions. So it should not be expected that a CF model can produce reliable values of CF parameters B_{kq}, allowing calculation of the ZFS parameters b_k^q, which in turn are very sensitive to B_{kq}.

Since for given symmetry case the number of the CF parameters B_{kq} is identical to that of the ZFS parameters b_k^q, the possibility arises of adjusting B_{kq} to fit b_k^q ($k=2$ and 4) without application of a specific CF model. This paper presents an attempt to achieve this goal. The spin-orbit coupling is treated as the only perturbation term, whereas the electrostatic and CF interactions are taken as the unperturbed Hamiltonian. Our calculations are carried out in the intermediate CF coupling scheme and take into account all the 252 states within the d^5 configuration, as described in Sec. II. As the spin-orbit energy is considerably smaller than the energies of excited quartets and doublets, measured from the ground ^6S state, the convergency is excellent. Microscopic derivations are consequently carried out for rank-2 as well as rank-4 ZFS parameters in cubic and tetragonal symmetries, in Secs. III and IV, respectively. Calculations are performed up to the fifth order. We shall show that the rank-2 terms come predominantly from second- and third-order perturbations, while the rank-4 terms mainly from fourth- and fifth-order perturbations. The behavior of each ZFS parameter—D, a, and F—are investigated in detail as function of the CF parameters B_{kq}. Applications are presented in Sec. V, where we consider Mn^{2+} and Fe^{3+} ions located at the cubic and axial (static and vacancy) sites in fluoroperovskites. The results are in good agreement with the observed EPR data for D, a, and F. Conclusions are given in Sec. VI.

II. THEORY

Let us consider a spin Hamiltonian in tetragonal symmetry[24,31] of the first kind (see Ref. 24), i.e., for the point groups C_{4v}, D_4, D_{2d}, and D_{4h},

$$\mathcal{H}_s=\tfrac{1}{3}b_2^0O_2^0+\tfrac{1}{60}(b_4^0O_4^0+b_4^4O_4^4)\ , \tag{1}$$

where $O_k^q(S_x,S_y,S_z)$ are Stevens[32] operators and the z axis is taken to be along the C_4 axis. The SH parameters b_k^q are related to the D, a, and F used conventionally in the literature by the relations[24,31]

$$\begin{aligned} b_2^0&=D\ ,\\ b_4^0&=\frac{a}{2}+\frac{F}{3}\ ,\\ b_4^4&=\tfrac{5}{2}a\ . \end{aligned} \tag{2}$$

Solving the Hamiltonian (1) within the basis of states $|S=\frac{5}{2},M_s\rangle$, we obtain the following formulas to be used in the derivation of the microscopic relations:

$$\begin{aligned} b_2^0&=\tfrac{1}{28}[5W(\tfrac{5}{2},\tfrac{5}{2})-W(\tfrac{3}{2},\tfrac{3}{2})-4W(\tfrac{1}{2},\tfrac{1}{2})]\ ,\\ b_4^0&=\tfrac{1}{14}[W(\tfrac{5}{2},\tfrac{5}{2})+2W(\tfrac{1}{2},\tfrac{1}{2})-3W(\tfrac{3}{2},\tfrac{3}{2})]\ ,\\ b_4^4&=\sqrt{5}W(\tfrac{5}{2},-\tfrac{3}{2})\ , \end{aligned} \tag{3}$$

where $W(M_s,M_s')$ denotes $\langle SM_s|\mathcal{H}_s|SM_s'\rangle$.

We follow the procedure described earlier in Ref. 3 and consider the Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{\mathrm{CF}}+\mathcal{H}_{\mathrm{s.o.}}\ , \tag{4}$$

where $\mathcal{H}_0$ denotes the free-ion Hamiltonian, $\mathcal{H}_{\mathrm{CF}}$ the CF potential, and $\mathcal{H}_{\rm s.o.}$ the spin-orbit coupling. The Wybourne notation[33] for the CF potential is adopted:

$$\mathcal{H}_{\rm CF}=B_{20}C_0^{(2)}+B_{40}C_0^{(4)}+B_{44}(C_4^{(4)}+C_{-4}^{(4)}) , \tag{5}$$

where $C_q^{(k)}$ are the normalized spherical harmonics. It is convenient to define[3] the parameters $B'_{40}=B_{40}-(\frac{14}{5})^{1/2}B_{44}$ and $Dq=[B_{40}+(\frac{14}{5})^{1/2}B_{44}]/42$, which describe the departure from cubic symmetry. The parameters B'_{40} and B_{20} vanish identically in cubic symmetry, and thus they measure the tetragonal distortion.

Writing $\mathcal{H}_{\rm CF}$ as the sum of cubic V_c and low-symmetric $V_{\rm LS}$ parts, Blume and Orbach[25] suggested taking $(V_{\rm LS}+\mathcal{H}_{\rm s.o.})$ as a perturbation to $(\mathcal{H}_0+V_c)$ in calculating the rank-2 SH parameters of ^6S-state ions.[26] Watanabe[27] has considered the total CF potential, $\mathcal{H}_{\rm CF}=V_c+V_{\rm LS}$, as a perturbation together with the spin-orbit coupling in the calculation of the cubic a and axial D parameters for the ^6S-state ions. This Watanabe procedure was regarded by Sharma, Orbach, and Das[26] as an independent mechanism since Watanabe's incomplete calculation indicated the dependence $D\propto(B_{20})^2$, which did not appear in the lowest order of the BO procedure. In fact, Watanabe[27] and Sharma, Orbach, and Das[26] dealt with exactly the same problem by using different perturbation procedures. Complete calculations using the Watanabe procedure have recently been carried out up to sixth order[7,13] for cubic,[16] tetragonal,[3,4] and trigonal[3,7] symmetries, whereas up to fourth order for orthorhombic,[3,6] and triclinic symmetry[5] cases. However, since V_c is usually comparable in magnitude with $\mathcal{H}_0$, the convergency of this procedure has been seriously questioned.[30] This point has been clarified[3,13,14] for the rank-2 SH parameters.

It is worth noting that in the calculation of the SH parameters of d^n ($n=2$, 3, 7, 8) ions, Macfarlane[28] and Zdansky[29] (MZ) treated $V_{\rm LS}$, $\mathcal{H}_{\rm s.o.}$, and the off-diagonal part of $\mathcal{H}_0$ altogether as a perturbation using the strong-field coupling scheme basis. This perturbation technique has been successfully developed to calculate D, a, and F for ^6S-state ions in cubic[8] and tetragonal[3,9] symmetries. The resulting analytical expressions are of relatively simple form, and it turns out that the numerical results agree well with the diagonalization calculations.[3,13] The fact that the ground state ^6S is not affected directly by the crystal field allows us to include here the total CF potential, $\mathcal{H}_{\rm CF}=V_c+V_{\rm LS}$, in the unperturbed Hamiltonian together with $\mathcal{H}_0$. The perturbation Hamiltonian includes, therefore, the spin-orbit interaction $H_{\rm s.o.}$ only. Since the spin-orbit energy is considerably less than the energies of excited spin quartets and doublets, measured from the ground state ^6S, the convergency is excellent, as will be shown below.

The present calculations are carried out in the intermediate CF coupling scheme.[34,35] The basis functions $|d^N\alpha SL\Gamma\gamma\rangle$ transforming as components γ of irreducible representations Γ of a double-valued group G' and constructed as the linear combinations of products of symmetry-adapted[34] orbital $|d^N\alpha L\Gamma_l\gamma_l\rangle$ and spin $|d^N\alpha S\Gamma_s\gamma_s\rangle$ functions are adopted:

$$|d^N\alpha SL\Gamma\gamma\rangle=\sum_{\gamma_l}\sum_{\gamma_s}C(\Gamma_l\gamma_l\Gamma_s\gamma_s;\Gamma\gamma)\times|d^N\alpha L\Gamma_l\gamma_l\rangle|D^N\alpha S\Gamma_s\gamma_s\rangle , \tag{6}$$

where

$$\begin{aligned}|d^N\alpha L\Gamma_l\gamma_l\rangle&=\sum_{M_L}C(M_L;\Gamma_l\gamma_l)|d^N\alpha LM_L\rangle ,\\ |d^N\alpha S\Gamma_s\gamma_s\rangle&=\sum_{M_s}C(M_S;\Gamma_s\gamma_s)|d^N\alpha SM_S\rangle .\end{aligned} \tag{7}$$

The basis functions in (7) are constructed using the projection operator technique, while the Clebsch-Gordan coefficients in (6) are obtained from the tables.[36] Within the basis functions (6), the CF matrix elements are diagonal with respect to S, Γ_s, and γ_s, and the resulting CF matrices are actually the same as in the irreducible representations Γ_l of the normal (single-valued) group G. Thus the matrices are block diagonal in the representation Γ of G', whereas the spin-orbit interaction couples the blocks. The basic formulas are obtained as follows: for a CF Hamiltonian (see, e.g., Ref. 34),

$$\langle d^N\alpha SLM_SM_L|\mathcal{H}_{\rm CF}|d^N\alpha'S'L'M'_SM'_L\rangle=\delta_{M_SM'_S}\delta_{SS'}\sum_{k,q}B_{kq}\langle d||C^{(k)}||d\rangle(-1)^{L-M_L}\begin{bmatrix}L & k & L'\\ -M_L & q & M'_L\end{bmatrix}\langle d^N\alpha SL||U^{(k)}||d^N\alpha'S'L'\rangle , \tag{8}$$

and for the spin-orbit coupling,

$$\langle d^N\alpha SLM_SM_L|\mathcal{H}_{\rm s.o.}|d^N\alpha'S'L'M'_SM'_L\rangle=\langle d||l^{(1)}||d\rangle\zeta\sum_{q=-1}^{1}(-1)^{q+S+L-M_S-M_L}\times\begin{bmatrix}S & 1 & S'\\ -M_S & -q & M'_S\end{bmatrix}\begin{bmatrix}L & 1 & L'\\ -M_L & q & M'_L\end{bmatrix}\langle d^N\alpha SL||V^{(11)}||d^N\alpha'S'L'\rangle , \tag{9}$$

where (⋯) is the $3j$ symbol and ζ is the spin-orbit coupling constant. The values of 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 listed in Ref. 37. The intermediate CF coupling scheme is very suitable for $3d^N$ ions for which the CF potential is stronger than the spin-orbit interaction, since the nonzero CF matrix elements are grouped in a block-diagonal form.[14] Our present calculations take into account all states of the d^5 configuration, i.e., total number of 252 states.

It is easy to show that when the spin-orbit coupling is regarded as the only perturbation term, the second- and higher-order perturbations have nonzero contributions to the rank-2 ZFS parameters b_2^q, while fourth and higher orders affect the rank-4 terms b_4^q. The second-order perturbation contribution $b_2^{q(2)}$ to the rank-2 ZFS parameters b_2^q is proportional to ζ^2. The proportionality factor $F_0(2,q)$ is defined by $b_2^{q(2)}=F_0(2,q)\zeta^2$. In a similar way we obtain the third-order contribution as $b_2^{q(3)}=F_1(2,q)\zeta^3$. The same idea is suitable for the rank-4 ZFS parameters b_4^q. We obtain the fourth-order contribution as $b_4^q=F_0(4,q)\zeta^4$ and the fifth-order contribution as $b_4^q=F_1(4,q)\zeta^5$. In this way, in fact, we obtain two expansion series of ζ for b_2^q and b_4^q. We write them one after the other:

$$\begin{aligned} b_k^q &= b_k^{q(k)}+b_k^{q(k+1)}+\cdots \\ &= F_0(k,q)\zeta^k+F_1(k,q)\zeta^{k+1}+\cdots . \end{aligned} \tag{10}$$

This perturbation series are expected to have a good convergence because the matrix elements of $\mathcal{H}_{\rm s.o.}$ are two orders of magnitude smaller than the energy separations between the ground and excited states. In the following sections we shall show that the first two terms in (10) contribute most to b_k^q; i.e., we can approximate

$$b_k^q \cong b_k^{q(k)}+b_k^{q(k+1)} . \tag{11}$$

The d^5 configuration can be regarded either as five d electrons or five d holes.[8,9,27,38,39] This makes the diagonal matrix elements of the CF and spin-orbit interactions zero. It leads to the fact that any physical quantity for a d^5 ion remains unchanged when the signs of both the spin-orbit coupling constant ζ and CF parameters B_{kq} are inversed:[8,9,39]

$$b_k^q(B,C,B_{kq},\zeta)=b_k^q(B,C,-B_{kq},-\zeta) . \tag{12}$$

This requires that $F_0,F_2,\ldots,F_{2n}$ in (10) be even functions of B_{kq} and that $F_1,F_3,\ldots,F_{2n+1}$ be odd functions of B_{kq}.[8,9] This feature is very useful in deriving analytical expressions for the SH parameters of d^5 ions.

The spin quartet $^4T_1(P)$ is the only excited state that couples via $\mathcal{H}_{\rm s.o.}$ with the ground ^6S state.[37] Because of this, the $^4T_1(P)$ state plays the most important role in affecting the ZFS of ^6S-state ions among various excited states. Considering the spin doublets, we find that they contribute to the ZFS parameters at fourth and higher orders. Therefore the spin doublets must play a negligible role for the rank-2 ZFS parameters b_2^q, which results mainly from the second- and third-order perturbations [see Eq. (11)]. In other words, the parameters b_2^q arise predominantly from the second- and third-order effects of the spin-orbit interaction within the ground ^6S state and excited spin quartets. This conclusion enables one to omit the spin doublets in the diagonalization calculation of b_2^q.[13,14] However, the spin doublets are non-negligible in the calculation of rank-4 ZFS terms,[8,9,15,16,39–42] although they have energies generally higher than the spin quartets.[27]

Therefore a successful comprehensive approach to the ZFS parameters b_k^q ($k=2$ and 4) should include all the 252 states within d^5 configuration and be carried out up to the fifth or higher orders. This is achieved in a numerical way in a FORTRAN program developed by us for tetragonal symmetry. Using the functions (6), the program computes the CF Hamiltonian and spin-orbit coupling matrices of Γ_6 (62×62) and Γ_7 (64×64) representations using (8) and (9). The input parameters are B, C, α (the Trees correction), B_{20}, B'_{40}, Dq, and ζ. The program outputs the respective contributions to the parameters b_2^0, b_4^0, and b_4^4, as well as the corresponding ones to the conventional parameters D, F, and a arising from second- up to fifth-order perturbations. The program is applicable to cubic symmetry by assuming $B_{20}=B'_{40}=0$. It takes about 3 min of CPU time for one set of computations. A copy of the program can be obtained from one of the authors (Yu) upon request.

III. ZERO-FIELD SPLITTING IN CUBIC SYMMETRY

In cubic symmetry there is only one ZFS parameter a, which relates to the separation between the Γ_8 and Γ_7 energy levels of the ground ^6S state by $3a=E(\Gamma_8)-E(\Gamma_7)$.[31] Thus it can be evaluated by means of diagonalization, as has also been done in Refs. 8, 15, 40, and 42. Perturbation calculations have also been performed, using the Watanabe[27] and MZ (Refs. 28 and 29) procedures, and analytical expressions have been available.[8,16] It should be mentioned that Powell, Gabriel, and Johnston[39] performed a perturbation calculation up to sixth order in a way similar to the one adopted in this paper. (Note that Dq in Table I of Ref. 39 should be replaced by $-Dq$.[8,15]) Powell, Gabriel, and Johnston[39] found that the spin-spin coupling contributes a negligible value to a in comparison with the contribution resulting from the spin-orbit coupling. The spin-orbit and CF interactions within the ground ^6S and excited $^4T_1$, $^2T_2$, and ^2E states are found to be the major source of the cubic ZFS.[8]

In previous work[8] we have made diagonalization calculations, which produce "accurate" values arising from the CF and spin-orbit interactions within the whole d^5 configuration for a given set of parameters. It has been concluded that $a^{(4)}=F_0\zeta^4$ is an even function, whereas

TABLE I. Cubic zero-field splitting parameter a (in 10^{-4} cm^{-1}) vs Dq for Fe^{3+} ions, calculated assuming $B=900$, $C=3300$, and $\zeta=400$ (in cm^{-1}).

Dq (cm^{-1})	$a^{(4)}$	$a^{(5)}$	a (total)	a (dia.)[a]	a (MZ)[b]
1600	130.1	24.8	154.9	155	118.0
1400	63.0	11.4	74.4	74.3	62.3
1200	32.9	6.1	39.0	39.0	34.7
1000	17.6	3.6	21.2	21.2	19.5
800	9.3	2.2	11.5	11.5	10.8
600	4.5	1.4	5.9	5.9	5.5
400	1.8	0.8	2.6	2.6	2.4
200	0.43	0.37	0.8	0.8	0.6
0	0	0	0	0	0
−200	0.43	−0.37	0.06	0.06	0.3
−400	1.8	−0.8	1.0	1.0	1.7
−600	4.5	−1.4	3.1	3.1	4.4
−800	9.3	−2.2	7.1	7.1	9.0
−1000	17.6	−3.6	14.0	14.0	16.7
−1200	32.9	−6.1	26.8	26.8	29.7
−1400	63.0	−11.4	51.6	51.7	53.3
−1600	130.1	−24.8	105.3	105.3	99.7

[a] Calculated by direct diagonalization (Ref. 8).

[b] Calculated using the Macfarlane-Zdansky perturbation procedure (Ref. 9).

$a^{(5)}=F_1\zeta^5$ is an odd function of Dq and that $a\cong a^{(4)}+a^{(5)}$. Here we present a direct confirmation of these findings. The results of the calculations carried out up to fifth order are displayed in Table I. It is indicated that $a^{(4)}(Dq)=a^{(4)}(-Dq)\gg a^{(5)}(Dq)>0$ for $Dq>0$, while $a^{(5)}(Dq)=-a^{(5)}(-Dq)$. We also note that the value of $a^{(4)}+a^{(5)}$ is very close to a evaluated by means of diagonalization within the accuracy (10^{-5} cm^{-1}) of computation. The calculated results are also compared with those obtained previously[8] using the MZ procedure. It is seen that the present procedure works well for a wide range of values of Dq.

IV. ZERO-FIELD SPLITTING IN TETRAGONAL SYMMETRY

It has been found that the contribution arising from the tetragonal CF components B_{20} and B'_{40} to the cubic ZFS parameters a is non-negligible.[9] This contribution is denoted with a_t so that[9]

$$a=a_c+a_t , \tag{13}$$

where a_c refers to the contribution arising purely from the cubic CF part. When the symmetry is increased from tetragonal to cubic, a_t vanishes and a equals to a_c. Since

TABLE II. Zero-field splitting parameter $b_2^0=D$ (in 10^{-4} cm^{-1}) vs Dq for Mn^{2+} ions in tetragonal symmetry, calculated assuming $B=911$, $C=3273$, $\alpha=65$, $\zeta=337$, $B_{20}=-1000$, and $B'_{40}=1000$ (in cm^{-1}).

	Present work							
Dq (cm^{-1})	$D^{(2)}$	$D^{(3)}$	$D^{(4)}$	D	D (BO)[a]	D (Watanabe)[b]	D (MZ)[c]	D (dia.)[d]
400	−70	13	−0.0	−57	−69	−58	−66	−83
500	−89	13	−0.0	−76	−88	−79	−78	−103
600	−109	13	−0.0	−95	−109	−100	−105	−124
700	−131	14	−0.1	−117	−131	−123	−126	−147
800	−155	15	−0.1	−140	−156	−148	−150	−172
900	−182	15	−0.1	−167	−184	−175	−176	−200
1000	−212	16	−0.1	−196	−215	−206	−206	−232
1100	−246	17	−0.1	−230	−250	−239	−240	−268
1200	−287	17	−0.2	−270	−291	−276	−280	−309
1300	−334	18	−0.3	−316	−340	−316	−327	−359
1400	−391	20	−0.4	−372	−397	−360	−383	−418
1500	−458	21	−0.7	−437	−467	−408	−451	−489

[a] Lowest-order calculation of the Blume-Orbach procedure (see Refs. 3, 26, and 13).

[b] Two lowest-order (fourth and sixth) calculations of the Watanabe-procedure (see Refs. 3 and 13).

[c] Lowest-order (third) calculation of the Macfarlane-Zdansky procedure (Refs. 3 and 13).

[d] Calculated by direct diagonalization (omitting the spin doublets) (Ref. 13).

a_c has been in Sec. III, we shall deal with a_t in this section together with the axial parameters D and F.

A. Rank-2 ZFS parameter D

The axial ZFS term D has been extensively studied during the past decades because of its significance in the EPR spectra (see Refs. 1–3). The fact that the axial CF component B_{20} does not appear in the lowest (third) nonzero order of the BO procedure[25] indicates the importance of B'_{40} in affecting D in tetragonal symmetry.[2] Figure 1 shows D as functions of B_{20}, B'_{40}, and Dq. It is seen from Fig. 1(a) that D depends quadratically on B_{20}. This dependence arises partially from the fourth-order processes involving B_{20} in the Watanabe[27] procedure as follows from the relation derived earlier:[5,27]

$$D(B_{20}) = -\frac{3\zeta^2[(B_{20})^2+21\zeta B_{20}]}{70(7B+7C)^2(17B+5C)} \ . \tag{14}$$

It is shown by the dot-dashed line in Fig 1(a). The term $D \propto (B_{20})^2$ in (14) was first given by Watanabe[27] and was referred to as the "Watanabe mechanism" in the earlier literature.[26] Figure 1(b) indicates a nearly linear B'_{40} dependence of D, as expected either from the BO or from the Watanabe procedure.[3,26] Figure 1(c) shows that the Watanabe perturbation procedure does not work so well as the BO one for $|Dq| > 1200$ cm^{-1} and that D is more sensitive to B'_{40} than to B_{20}.

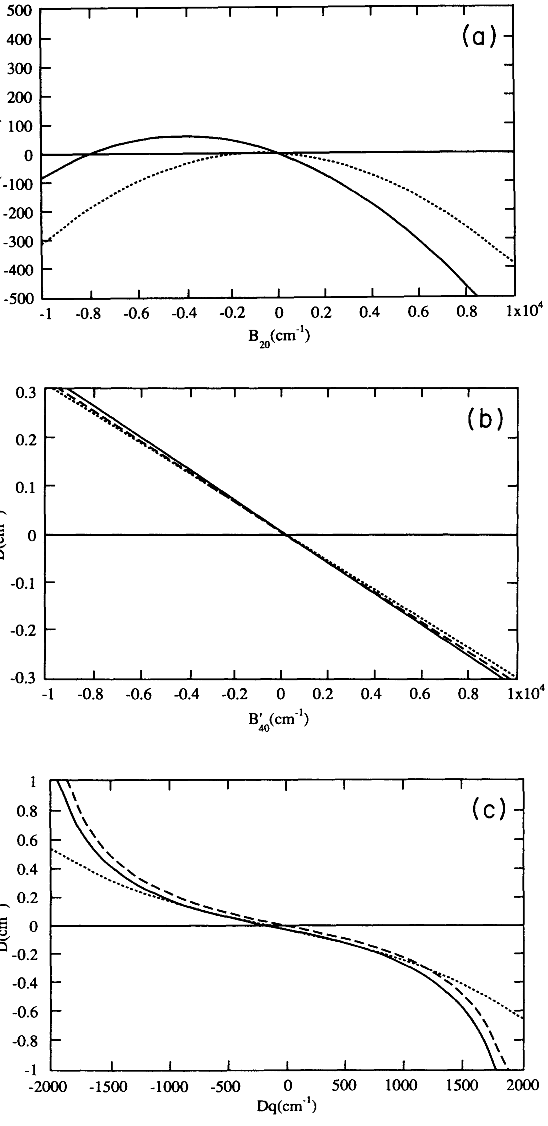

FIG. 1. Axial spin Hamiltonian parameter D for Fe^{3+} ions ($B=900$, $C=3300$, and $\zeta=400$ in cm^{-1}) in tetragonal symmetry, as a function of (a) B_{20} ($Dq=1000$ cm^{-1} and $B'_{40}=0$), (b) B'_{40} ($B_{20}=0$ and $Dq=1000$ cm^{-1}), and (c) Dq ($B_{20}=B'_{40}=7000$ cm^{-1}). The results calculated using the Watanabe (dot-dashed lines) and Blume-Orbach (dashed lines) procedures are shown for comparison.

In Table II we display the distinct contributions of the first three (second, third, and fourth) orders of perturbation, together with a comparison with values calculated by BO, MZ, and Watanabe perturbation procedures. We note the approximation given by (14), i.e., $D \cong D^{(2)}+D^{(3)}$. The conclusion that the rank-2 ZFS parameters b_2^q arise predominantly from the combined CF and spin-orbit interactions among the ground ^6S and spin quartets is plausible from perturbation processes such as the ones given by Eqs. (10) and (11). It is also clear that the spin doublets cannot contribute to D in the second and third orders, which produce the major part of D. Table II indicates a consistency among the perturbation procedures considered.

A great deal of effort has been afforded to evaluate D (or b_2^0) by diagonalization of the full energy matrices.[3,11–14,35,43,44] However, such calculations can only produce approximate results. In tetragonal symmetry the three ZFS parameters b_2^0, b_4^0, and b_4^4 cannot be uniquely deduced from the three energy levels $[E(M_s=\pm\frac{5}{2})$, $E(M_s=\pm\frac{3}{2})$, and $E(M_s=\pm\frac{1}{2})]$ in the ground ^6S state. A commonly used approximation is to omit b_4^4 (or a) in the spin Hamiltonian (1), which becomes then diagonal with respect to the basis $|^6S,M_s\rangle$. This approximation is reasonable in the case of strong distortion, where $a \ll |D|$. Thus two relations involving b_2^0 can be derived in this case:

$$\begin{aligned} b_2^{0'} &= \tfrac{1}{4}[E(\pm\tfrac{5}{2})-E(\mp\tfrac{3}{2})] \cong b_2^0+b_4^0 \ , \\ b_2^{0''} &= \tfrac{1}{2}[E(\pm\tfrac{3}{2})-E(\mp\tfrac{1}{2})] \cong b_2^0-\tfrac{5}{2}b_4^0 \ . \end{aligned} \tag{15}$$

Relationships (15) are correct for trigonal symmetry as well. Further neglecting b_4^0 in (15), previous works[3,11–14,35,43–45] adopted either $b_2^{0'}$, or $b_2^{0''}$, or $(b_2^{0'}+b_2^{0''})/2$ to approximate b_2^0. The resultant errors are then in the order of b_4^q/b_2^0, which would reach 15%, as can be seen from Table II.

B. Rank-4 ZFS parameters a and F

There have appeared but a few papers dealing with the rank-4 ZFS parameters of ^6S-state ions, possibly because of the considerably tedious calculations. Sato, Rispin, and Kon[45] considered the contribution of only two excited states. More recently, a fifth-order perturbation calcu-

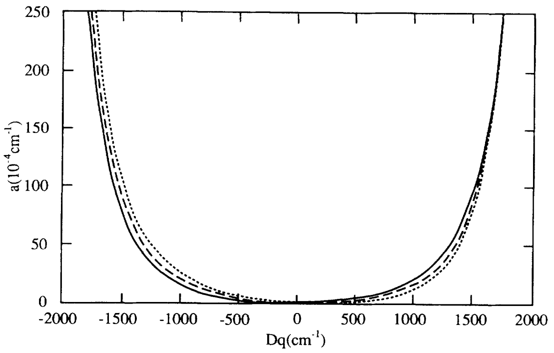

FIG. 2. Cubic parameter a vs Dq. The value of B, C, and ζ are as in Fig. 1. Solid line, $B_{20}=B'_{40}=0$; dashed line, $B_{20}=B'_{40}=4000\ \mathrm{cm}^{-1}$; dot-dashed line, $B_{20}=B'_{40}=7000\ \mathrm{cm}^{-1}$.

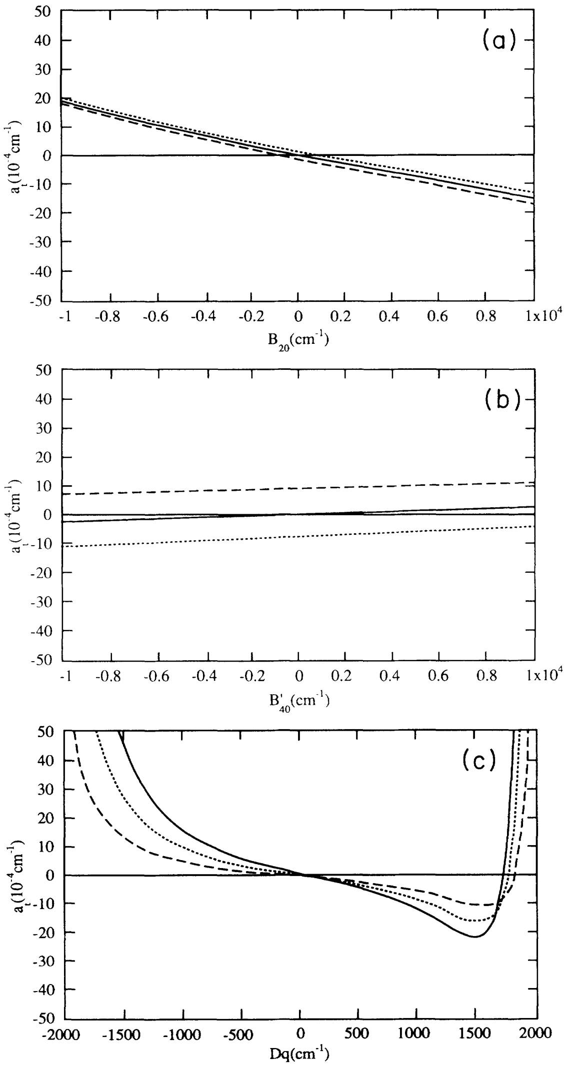

FIG. 3. Contribution a_t vs (a) B_{20} [$Dq=1000\ \mathrm{cm}^{-1}$ and $B'_{40}=0$ (solid line), $Dq=1000\ \mathrm{cm}^{-1}$ and $B'_{40}=-5000\ \mathrm{cm}^{-1}$ (dashed line), and $Dq=1000\ \mathrm{cm}^{-1}$ and $B'_{40}=5000\ \mathrm{cm}^{-1}$ (dot-dashed line)]; (b) B'_{40} [$Dq=1000\ \mathrm{cm}^{-1}$ and $B_{20}=0$ (solid line), $Dq=1000\ \mathrm{cm}^{-1}$ and $B_{20}=-5000\ \mathrm{cm}^{-1}$ (dashed line), and $Dq=1000\ \mathrm{cm}^{-1}$ and $B_{20}=5000\ \mathrm{cm}^{-1}$ (dot-dashed line)]; and (c) Dq [$B_{20}=B'_{40}=4000\ \mathrm{cm}^{-1}$ (dashed line), $B_{20}=B'_{40}=7000\ \mathrm{cm}^{-1}$ (dot-dashed line), and $B_{20}=B'_{40}=10\,000\ \mathrm{cm}^{-1}$ (solid line)].

lation has been carried out and analytical expressions have been derived by taking into account all excited states in the MZ procedure.[9] The effect of the tetragonal CF components on the cubic ZFS parameter a_t has been found to be non-negligible, and an approximate relation $a_t/F \cong -\frac{1}{2}$ has been derived.[9] We shall show in this subsection that this relation is only approximate, whereas the derived analytical formulas do not work so well as one would expect.

Figure 2 shows a versus Dq and indicates a sensitive dependence. The a_t and F parameters are plotted in Figs. 3 and 4, respectively. It is seen from the Fig. 2 that a has a Dq dependence similar to that of a_c. In the literature the power law $a \propto (Dq)^k$ and $a \propto R^{-m}$, which define the factors k and m, were frequently adopted (see, e.g., Refs. 46–48). It has been realized that the exponent k is a function of Dq:[8]

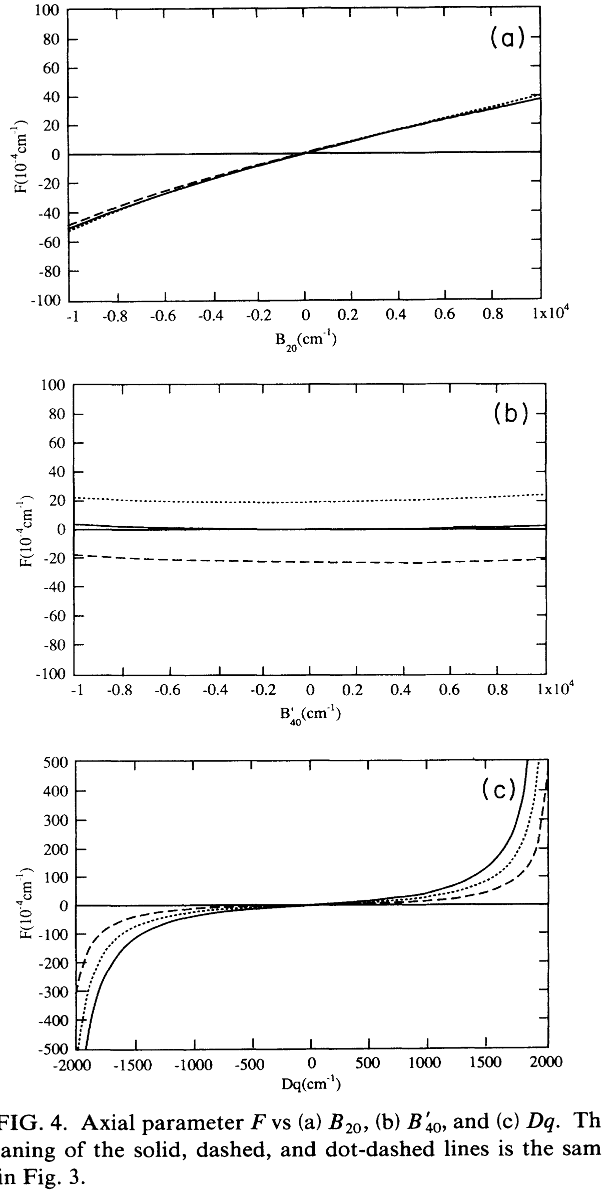

FIG. 4. Axial parameter F vs (a) B_{20}, (b) B'_{40}, and (c) Dq. The meaning of the solid, dashed, and dot-dashed lines is the same as in Fig. 3.

$$k \cong \Delta[2/(10B+6C+12\alpha-\Delta) + 2/(15B+10C+22\alpha-2\Delta) + 1/(\Delta-C/3)] , \quad (16)$$

where α is the Trees correction and $\Delta=|10Dq|$. For Mn^{2+} ions the values of k are around 2 in weak and intermediate CF and may reach 4 or even greater in strong CF.[8] The values of k are usually greater for Fe^{3+} than for Mn^{2+} ions because of the greater CF strength in Fe^{3+} cases. The value of m, however, can then be calculated using the equation[8] $m=kn$, where n is defined by $Dq \propto R^{-n}$, R being the interatomic distance of a given crystal. As the consequence of the fact that k is a function of Dq, m depends on the interatomic distance R of the crystal.[8]

It is seen from Figs. 3(a) and 4(a) that a_t and F are both sensitive in a nearly linear way to the rank-2 axial CF parameter B_{20}. On the other hand, we note from Figs. 3(b) and 4(b) that a_t and F are insensitive to the rank-4 axial CF parameter B'_{40}. Figures 3(c) and 4(c) illustrate that both a_t and F change sign with the change in sign of Dq. In particular, F seems to be an odd function of Dq, although not exactly, as indicated in the Table III. Figure 5 shows the behavior of the ratio a_t/F. As has been found previously,[9] the ratio a_t/F is insensitive to all CF parameters B_{20}, B'_{40}, and Dq and range from -0.2 to -0.5. Table III displays the distinct contributions of the fourth and fifth order to a_t and F as well as provides a comparison with the previous theory.[9] A very good convergency is obtained in the case of both a_t and F. The MZ procedure does not work so well as we expected, as can be seen from the comparison between the columns a_t and a_t(MZ) and between F and F(MZ). In the lowest-(fifth-) order calculation, the previous work predicted $a_t(Dq)=-a_t(-Dq)$ and $F(Dq)=-F(-Dq)$, implying $a_t(Dq=0)=0$ and $F(Dq=0)=0$.[9] These relations hold indeed quite well in the case of F, i.e., $F(Dq)\cong -F(-Dq)$, but not so well in the case of a_t. This feature can be observed in Figs. 3(c) and 4(c) as well.

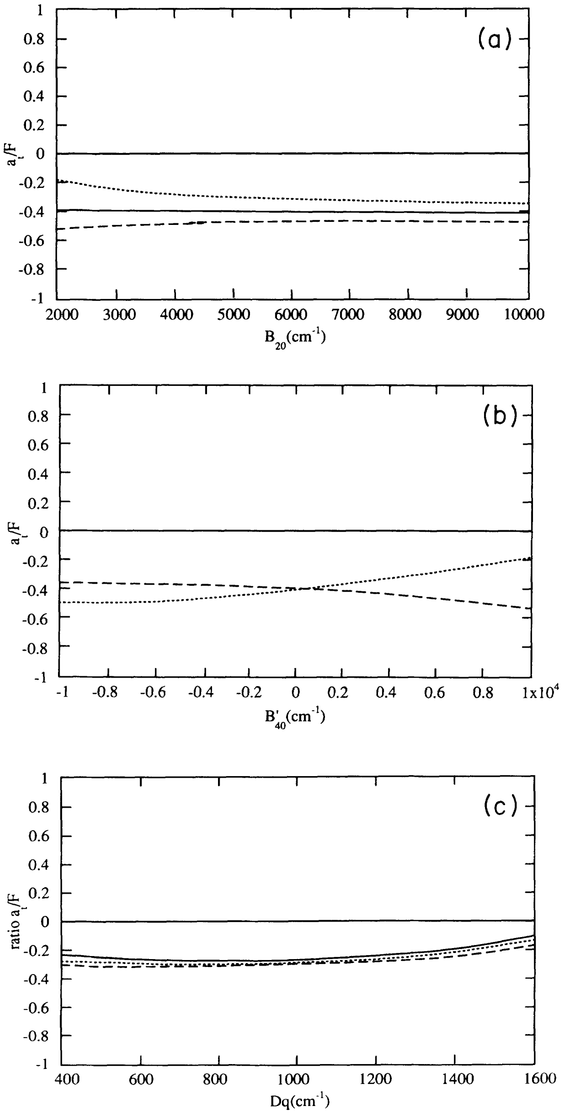

FIG. 5. Ratio a_t/F vs (a) B_{20}, (b) B'_{40}, and (c) Dq. The meaning of the lines used is the same as in Fig. 3.

V. APPLICATIONS

Numerical calculations in earlier works[2–23,25–27,38–45] concerned either the rank-2 (D) or rank-4 (the cubic a) ZFS parameters. The theory presented in this paper enables calculation of both the rank-2 and rank-4 parameters comprehensively. This is of significance since the parameters which are used in the calculation of the rank-2 ZFS parameters must also account for the rank-4 terms as well, and thus a better correlation can be obtained.

Considering the ZFS of ^6S-state ions as a consequence of the combined effect of the spin-orbit and CF interactions within the whole d^5 configuration, we obtain that each ZFS parameter is related to the spin-orbit coupling constant ζ and CF parameters B_{kq}, as well as the electrostatic parameters B and C. Thus the ZFS parameters are intercorrelated. The weak CF effect on the excited states makes it rather difficult to gain information about the CF parameters except that on Dq. When the rank-2 or -4 ZFS parameters are studied separately, one has to use a specific CF model since the number of unknown CF parameters is more than that of the ZFS parameters. The theory presented here allows us to calculate all the ZFS parameters b_k^q ($k=2$ and 4) by regarding all the CF parameters B_{kq} ($k=2$ and 4) as adjustable phenomenological parameters, providing the values of the electrostatic and spin-orbit parameters are available. This constitutes the essential idea for the numerical calculations presented below.

A. Mn^{2+} and Fe^{3+} ions in cubic fluoroperovskites

The Mn^{2+} and Fe^{3+} ions in cubic fluoroperovskites, which are typical regular octahedral lattices, provide good examples for the examination of the microscopic SH theory of ^6S-state ions. In cubic symmetry there is only one CF (Dq) and one ZFS (a) parameter.

TABLE III. Zero-field splitting parameters a_t and F (in 10^{-4} cm^{-1}) vs Dq for Fe^{3+} ions ($B=900$ cm^{-1}, $C=3300$ cm^{-1}, and $\zeta=400$ cm^{-1}).

Dq (cm^{-1})	$a_t^{(4)}$	$a_t^{(5)}$	a_t	a_t (MZ)[a]	$F^{(4)}$	$F^{(5)}$	F	F (MZ)[a]
−1600	58.4	−1.0	57.4	33.5	−158.6	5.3	−153.3	−86.1
−1400	36.1	−0.9	35.2	16.9	−96.3	3.6	−92.7	−43.5
−1200	24.1	−0.8	23.3	9.7	−63.1	2.7	−60.4	−24.8
−1000	16.8	−0.7	16.1	5.9	−43.0	2.1	−40.9	−15.2
−800	12.0	−0.6	11.4	3.8	−29.7	1.8	−27.9	−9.7
−600	8.6	−0.5	8.1	2.4	−20.3	1.6	−18.7	−6.1
−400	5.9	−0.5	5.4	1.4	−13.0	1.4	−11.6	−3.6
−200	3.7	−0.4	3.3	0.7	−7.0	1.4	−5.6	−1.7
0	1.7	−0.4	1.3	0	−1.5	1.3	−0.2	0
200	−0.2	−0.5	−0.7	−0.7	4.1	1.4	5.5	1.7
400	−2.3	−0.4	−2.7	−1.4	10.2	1.5	11.7	3.6
600	−4.7	−0.5	−5.2	−2.4	17.7	1.7	19.4	6.1
800	−7.6	−0.4	−8.0	−3.8	27.6	1.9	29.5	9.7
1000	−11.6	−0.3	−11.6	−5.9	41.8	2.4	44.2	15.2
1200	−16.2	0.1	−16.1	−9.7	64.1	3.1	67.2	24.8
1400	−21.8	1.5	−20.3	−16.9	102.9	4.4	107.3	43.5
1600	−24.4	6.8	−17.6	−33.5	180.1	7.0	187.1	86.1

[a] Lowest-order (fifth) calculation of the MZ procedure (Ref. 9).

Let us first consider Mn^{2+}:KZnF$_3$. It has been reported that $Dq=822$ cm^{-1}, $B=830$ cm^{-1}, $C=3122$ cm^{-1}, and $\alpha=76$ cm^{-1} from a least-squares fitting to the optical-absorption peaks[49] and that $a=(6.3\pm1)\times10^{-4}$ cm^{-1} from EPR experiments.[50] Only the values of the spin-orbit coupling constant ζ was unknown for Mn^{2+} ions in this compound, and we treat it as an adjustable parameter fitting the observed ZFS value. We obtain $\zeta=324$ cm^{-1}, which compares well with the calculated[51] free-ion value of 333 cm^{-1}.

In order to evaluate the ZFS of Mn^{2+} ions in other fluoroperovskites, for which optical measurements are not available, we assume that they have values of B, C, α, and ζ identical to those of Mn^{2+}:KZnF$_3$. Later, we will assume that all the cubic and tetragonal fluoroperovskites under investigation have the same that values of B, C, α, and ζ when they are doped with Mn^{2+}. This assumption seems to be quite reasonable in our case, because of similar crystalline structure[49] in all fluoroperovskites under consideration. For example, it has been reported that $B=825$ cm^{-1} and $C=3136$ cm^{-1} for Mn^{2+}:RbCdF$_3$, as compared with $B=830$ cm^{-1} and $C=3122$ cm^{-1} found for Mn^{2+}:KZnF$_3$.[49] The slight difference in the values of these parameters for the lattices under consideration will make the calculated results somewhat different, but will not cause a change in the final conclusions. We then adjust Dq to fit the observed ZFS parameter a. The calculated and observed[50,52,53] results are listed in Table IV. The deduced value of $Dq=730$ cm^{-1} is in good agreement with $Dq=715$ cm^{-1} obtained from optical data.[49] Thus we expect that other Dq values deduced in this way will also be reasonable.

The case of Fe^{3+} ions is somewhat complicated because of a lack of detailed optical data. Since a predominant amount of Fe ions in Fe:KZnF$_3$ crystals appears to be the 2+ state when Fe ions replace Zn^{2+} ions in this crystal, it is difficult to observe optical lines due to Fe^{3+}. Fortunately, in the large-Fe-concentration samples of KZn$_x$Fe$_{1-x}$F$_3$, five sharp absorption lines around 25 800 cm^{-1} have been found and attributed to the transitions from $^6A_{1g}$ to the degenerate states $^4A_{1g}(^4G)$ and $^4E_g(^4G)$. Another band centered around 29 000 cm^{-1} has been attributed to the transitions from $^6A_{1g}$ to $^4T_{2g}(^4D)$.[54] This feature is very similar to that seen in Li$_3$Na$_3$Fe$_2$F$_{12}$ crystals, where for the Fe^{3+} ions the values $B=877.5$ cm^{-1}, $C=3146$ cm^{-1}, and $\alpha=64.5$ cm^{-1} have been obtained.[54]

TABLE IV. Zero-field splitting parameter a for Mn^{2+} ions in cubic sites of fluoroperovskites; $B=830$, $C=3122$, $\alpha=76$, and $\zeta=324$ (in cm^{-1}) for all the compounds as well as the Dq values listed in the first row are assumed.

	Mn^{2+}:RbCaF$_3$	Mn^{2+}:TlCdF$_3$	Mn^{2+}:KCdF$_3$	Mn^{2+}:RbCdF$_3$	Mn^{2+}:KMgF$_3$	Mn^{2+}:KZnF$_3$
Dq (cm^{-1})	693	723	743	730	833	822
$a^{(4)}$ (10^{-4} cm^{-1})	3.4	3.8	4.0	3.9	5.5	5.3
$a^{(5)}$ (10^{-4} cm^{-1})	0.7	0.8	0.9	0.8	1.0	1.0
a (total) (10^{-4} cm^{-1})	4.1	4.6	4.9	4.7	6.5	6.3
a (expt.) (10^{-4} cm^{-1})	4.1(2)	4.6(2)	4.9(3)	4.7(2)	6.5(5)	6.3(1)
Ref. for a (expt.)	53	53	53	53	52	50

TABLE V. Zero-field splitting parameters for Fe^{3+} ions in cubic sites of fluoroperovskites; $B=877.5$, $C=3146.5$, $\alpha=64.5$, and $\zeta=371$ (in cm^{-1}) for all the compounds as well as the Dq values listed in the first row are assumed.

	Fe^{3+}:TlCdF$_3$	Fe^{3+}:RbCdF$_3$	Fe^{3+}:KCdF$_3$	Fe^{3+}:KZnF$_3$	Fe^{3+}:KMgF$_3$	Fe^{3+}:RbCaF$_3$
Dq (cm^{-1})	1295	1297	1350	1348	1340	1254
$a^{(4)}$ (10^{-4} cm^{-1})	37.6	37.9	45.2	44.8	43.6	32.9
$a^{(5)}$ (10^{-4} cm^{-1})	6.6	6.6	7.8	7.8	7.6	5.8
a (total) (10^{-4} cm^{-1})	44.2	44.5	53.0	52.6	51.2	38.7
a (expt.) (10^{-4} cm^{-1})	44.1(2)	44.5(2)	53(2)	52.7(2)	51.2(5)	38.7(3)
Ref. for a (expt.)	56	56	52	50	52	46

We assume that Fe^{3+} ions in $KZnF_3$ as well as in all fluoroperovskites have values of B, C, or ζ close to those for $Li_3Na_3Fe_2F_{12}$ crystals.

Recently, photoluminescence lines have been observed for Fe^{3+} ions in $KMgF_3$ crystals at 14 309, 14 288, 14 260, and 14 239 (in cm^{-1}), due to $^4T_{1g}(g)\Longrightarrow {}^6A_{1g}$ transitions.[55] We thus obtain $Dq=1340$ cm^{-1} for Fe^{3+}:KMgF$_3$. The calculated results are as follows: 14 270 cm^{-1} for $^4T_{1g}$, 19 890 cm^{-1} for $^4T_{2g}$, 25 800 cm^{-1} for $^4A_{1g}$ and ^4E_g, and 28 560 cm^{-1} for $^4T_{2g}$, as measured from $^6A_{1g}$. We thus obtain $B=877.5$, $C=3146.5$, $\alpha=64.5$, and $Dq=1340$ (in cm^{-1}) for Fe^{3+}:KMgF$_3$. Adjusting ζ to fit the observed[52] value of a, we obtain $\zeta=371$ cm^{-1}, which is much less than the calculated[51] free-ion value of 486 cm^{-1}. Assuming that Fe^{3+} ions in all fluoroperovskites have the same value of B, C, ζ, and α, we are able to calculate the ZFS parameter a by regarding Dq as an adjustable parameter to fit the observed values[46,50,52,56] as we did in the Mn^{2+} case. The results are shown in Table V. It is noted that a strong Jahn-Teller effect occurs within the $^4T_{1g}$ multiplet of Fe^{3+}:KMgF$_3$.[55] The spin-orbit energies of $^4T_{1g}(P)$ have been calculated by us as 13 971, 14 133, 14 267, and 14 337 (in cm^{-1}). The spacing of the splitting is 365 cm^{-1}. However, the four energy levels of $^4T_{1g}(P)$ have been found[55] experimentally to be 14 239, 14 260, 14 288, and 14 309 (in cm^{-1}) with a splitting spacing of 70 cm^{-1}.

B. Mn^{2+} and Fe^{3+} ions at tetragonal centers in fluoroperovskites

In tetragonal symmetry there are three CF parameters B_{20}, B'_{40}, and Dq and three ZFS parameters D, a, and F.

TABLE VI. Zero-field splitting parameters for Mn^{2+} ions in tetragonal centers of fluoroperovskites; $B=830$, $C=3122$, $\alpha=76$, and $\zeta=324$ (in cm^{-1}) for all the compounds as well as values of the CF parameters listed in the first three rows are assumed.

		Rb_2CdF_4	K_2CdF_4	Rb_2MgF_4	Rb_2ZnF_4	K_2MgF_4	K_2ZnF_4
B_{20} (cm^{-1})		−1500	6000	2000	2450	7500	1400
B'_{40} (cm^{-1})		−280	−1280	50	150	−2000	−360
Dq (cm^{-1})		730	743	833	822	833	822
D (10^{-4} cm^{-1}):	second	36.5	114.7	−19.3	−41.9	227.3	58.7
	third	24.3	−92.1	−33.4	−40.7	−119.3	−22.7
	fourth	−2.3	0.6	0.3	0.4	0.9	0.2
	fifth	0.1	−0.3	−0.1	−0.1	−0.5	−0.1
	total	60.6	22.9	−52.5	−82.3	108.4	36.1
	expt.	60.2(7)	21.2(10)	−53.2(5)	−81.4(8)	107.0(2)	36.0(2)
F (10^{-4} cm^{-1}):	fourth	−1.9	7.1	3.0	3.6	10.8	2.1
	fifth	0.0	−0.1	0.0	0.0	−0.2	−0.0
	total	−1.9	7.0	3.0	3.6	10.6	2.1
	expt.	−0.7(20)	6.5(18)	1.8(15)	3.5(30)	11.0(2)	1.9(6)
a (10^{-4} cm^{-1}):	fourth	4.6	1.0	4.3	3.9	0.7	4.5
	fifth	0.8	0.9	1.1	1.0	1.1	1.0
	total	5.4	1.9	5.4	4.9	1.8	5.5
	expt.	6.1(9)	1.6(8)	5.3(5)	3.2(15)	2.0(1)	5.6(2)
a (10^{-4} cm^{-1})		+0.7	−3.0	−1.1	−1.4	−4.7	−0.8
Ref. for D, F, a (expt.)		57	57	57	57	19	18

It is easy to make a comprehensive calculation of all the ZFS parameters by regarding the CF parameters as adjustable parameters under the assumption that the Mn^{2+} or Fe^{3+} ions in all the fluoroperovskites have the same value for the electrostatic as well as the spin-orbit coupling parameter for either ion.

We consider at first the Mn^{2+} ions in the tetragonal (D_{4h}) fluoroperovskites K_2MgF_4, K_2ZnF_4, Rb_2CdF_4, K_2CdF_4, Rb_2MgF_4, and Rb_2ZnF_4 for which the electron-nuclear double-resonance (ENDOR) and EPR experimental data are available.[18,19,57] The ZFS of Mn^{2+} ions in K_2MgF_4 and K_2ZnF_4 crystals has recently been calculated by Yu[9] using the MZ perturbation procedure, which does not work very well for F and a_t, as has been pointed out in Sec. III. In deriving the CF parameters used in these calculations, the superposition model[58] of crystal fields has been applied and crystallographic data derived from the experimental data[59] of superhyperfine constants were adopted. The agreement obtained between the calculated and observed results is reasonable, but also not quite satisfactory.

In our present calculation we assume that Rb_2CdF_4 and $RbCdF_3$ ($Dq = 730$ cm^{-1}), K_2CdF_4, and $KCdF_3$ ($Dq = 743$ cm^{-1}), Rb_2MgF_4, K_2MgF_4, and $KMgF_3$ ($Dq = 833$ cm^{-1}), and Rb_2ZnF_4, K_2ZnF_4, and $KZnF_3$ ($Dq = 822$ cm^{-1}) have the same Dq values (given in the parentheses above) as deduced in the Table IV. The electrostatic parameters and spin-orbit coupling constant are assumed to be the same as those for Mn^{2+}:$KZnF_3$, i.e., $B = 830$, $C = 3122$, $\alpha = 76$, and $\zeta = 324$ (in cm^{-1}) (Ref. 49 and Sec. V A). Thus we have two CF parameters B_{20} and B'_{40} left as adjustable parameters. The fittings were worked out noting that D is sensitive to B'_{40}, while a_t and F are also sensitive to B_{20}. However, the extensive FORTRAN program used in the calculation does not allow efficient least-squares fitting. Table VI presents a set of B_{20} and B'_{40}, which produces D, F, and a, agreeing well with the observed data.

A similar procedure was performed for Fe^{3+} ions at the vacancy centers of $RbCdF_3$,[60] $CsCdF_3$,[60] and $KZnF_3$ (Ref. 61) and the substitutional tetragonal center of Rb_2CdF_4.[62] We have assumed that the vacancy centers have the same value of Dq as the cubic centers. The results are shown in Table VII. The experimental errors are small, and the agreement between the calculated and observed results is very good.

It follows from the Tables VI and VII that the contributions to D from fourth- and fifth-order perturbations are negligible. The third-order perturbation plays a very important role, especially in the case of Mn^{2+} ions, where it contributes to D between 50% and 250% of the contribution resulting from the second-order perturbation. The fifth-order contribution to F is always negligible in the present cases. Tables VI and VII list also the calculated values of a_t. Its significance is obvious—the effect of the tetragonal field components on the cubic ZFS is non-

TABLE VII. Zero-field splitting parameters for Fe^{3+} ions in tetragonal centers of fluoroperovskites; $B = 877.5$, $C = 3146.5$, $\alpha = 64.5$, and $\zeta = 371$ (in cm^{-1}) for all the compounds as well as values of the CF parameters listed in the first three rows are assumed.

		$KZnF_3$	Rb_2CdF_4	$CsCdF_3$-Li^+	$CsCdF_3$-V_{Cd}	$RbCdF_3$-Li^+	$RbCdF_3$-V_{Cd}
B_{20} (cm^{-1})		4100	2700	5000	2850	4100	2600
B'_{40} (cm^{-1})		1020	530	1060	850	800	640
Dq (cm^{-1})		1348	1297	1297	1297	1297	1297
D (10^{-4} cm^{-1})	second	−615.8	−286.6	−628.2	−442.2	−462.9	−335.9
	third	−155.7	−95.9	−176.5	−103.5	−144.6	−93.4
	fourth	5.4	2.9	5.5	3.3	4.5	2.9
	fifth	−1.1	−0.6	−1.2	−0.7	−1.0	−0.6
	total	−767.2	−380.2	−800.4	−543.1	−604.0	−427.0
	expt.	−759.0(5)	−369.3(2)	−800.9(1)	−547.7(1)	−603.6(1)	−421.7(1)
F (10^{-4} cm^{-1})	fourth	31.5	18.4	33.5	19.2	27.7	17.6
	fifth	0.4	0.2	0.3	0.2	0.2	0.2
	total	31.9	18.6	33.8	19.4	27.9	17.8
	expt.	31.0(5)	20.9(3)	35.3(2)	19.5(2)	30.0(2)	18.0(2)
a (10^{-4} cm^{-1})	fourth	33.4	31.0	25.6	30.9	27.6	31.5
	fifth	7.8	6.6	6.6	6.6	6.6	6.6
	total	41.2	37.6	32.2	37.5	34.2	37.9
	expt.	39.0(5)	40.5(3)	34.3(2)	37.0(2)	36.0(2)	38.2(2)
a_t (10^{-4} cm^{-1})		−11.4	−6.9	−12.3	−7.0	−10.3	−6.6
Ref. for D, F, a (expt.)		61	62	60	60	60	60

negligible. In particular, for Mn^{2+}:K_2CdF_4 and Mn^{2+}:K_2MgF_4 crystals, the values of a_t are even greater in magnitude than the observed cubic ZFS parameter a.

VI. CONCLUSIONS

We have studied in detail the rank-2 and -4 zero-field splitting parameters of ^6S-state ions in cubic and tetragonal symmetries. The crystal field and electrostatic interactions have been taken as the unperturbed Hamiltonian, whereas the spin-orbit coupling has been taken as a perturbation. Since the derivation of analytical formulas in high orders of perturbation is too tedious, a FORTRAN program has been developed to calculate numerically the zero-field splitting parameters D, a, and F up to the fifth order within the whole d^5 configuration (252 states). Using this program, we have studied the cubic parameter a as well as the tetragonal parameters D, a, and F in a wide range of values of the crystal-field parameter Dq. The perturbation process shows a very good convergency as follows from comparison with the diagonalization results. The zero-field splitting parameters have also been studied as a function of the tetragonal crystal-field parameters B_{20} and B'_{40}. It has been found that the parameters B_{20} and B'_{40} contribute to the zero-field splitting parameter a, a value of a_t which is non-negligible for the cases under consideration. The parameters a_t and F are sensitive to the crystal-field parameter B_{20}, whereas D is sensitive to B'_{40}. The present theory has been applied to calculate the zero-field splitting parameters for Fe^{3+} and Mn^{2+} ions at the cubic (a) and tetragonal (a, F, and D) symmetries in fluoroperovskites. Since for the tetragonal symmetry the number of zero-field splitting parameters equals that of the crystal-field parameters, we have been able to regard the crystal-field parameters as adjustable phenomenological parameters. In this way we have avoided problems arising from application of a specific crystal-field model. The present results are in good agreement with the experimental EPR and ENDOR data. Our present study reveals that crystal-field theory provides a reasonable interpretation of the microscopic origin of the zero-field splitting of ^6S-state ions.

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