PHYSICAL REVIEW B VOLUME 49, NUMBER 5 1 FEBRUARY 1994-I

Theory of the zero-field splitting of $^6S(3d^5)$-state ions in cubic crystals

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(Received 18 May 1993; revised manuscript received 12 October 1993)

A study is made of the zero-field splitting (ZFS) of $^6S(3d^5)$ ions in cubic crystals, based on an extended crystal-field (CF) model which assumes two constants ζ_{te} and ζ_{tt} in the description of the spin-orbit (SO) interaction. In addition to the recognized origin for the ZFS, namely, the combined effect of the CF and the SO couplings, a second source is found to arise from the SO interaction alone through a difference between ζ_{te} and ζ_{tt} caused by covalency. To understand this second effect, we have investigated the SO coupling processes which contribute to the ZFS, using the Macfarlane-Zdansky perturbation procedure. Processes in which the couplings are all between states of different configurations $t_2^m e^{5-m}$ are found to make a positive contribution proportional to ζ_{te}^4. Other processes contribute negatively through a term in $\zeta_{te}^2\zeta_{tt}^2$. The ZFS is thus determined by the relative magnitudes of these two parts, and a small difference between ζ_{te} and ζ_{tt} will cause a great change in its value. Application of this new theory is successfully made to Mn^{2+} ions in tetrahedral II-VI compounds and in fluoroperovskites.

I. INTRODUCTION

As one of the most important spin-Hamiltonian parameters of a $^6S(3d^5)$-state ion, the cubic zero-field splitting (ZFS) parameter a is defined as[1] ($S=\frac{5}{2}$)

$$\mathcal{H}_s=(a/6)[S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)] . \tag{1}$$

In the framework of the crystal-field (CF) model, ZFS is interpreted as a combined effect of CF and spin-orbit (SO) couplings.[2-11] However, owing to the lack of orbital angular momentum in the ground state ^{6}S, calculation of a is rather complicated. Cubic symmetry is an easier case to deal with, where a is simply related to the energies of the Γ_7 and Γ_8 irreducible representations of the ground state $^6A_1$ by the relation[2] (the suffix g is omitted throughout this paper)

$$3a=E(\Gamma_8)-E(\Gamma_7) . \tag{2}$$

This equation indicates simultaneous diagonalization of electrostatic, CF, and SO interactions to be an effective way of calculating a. Based on this idea, calculations have been performed for many crystals containing Mn^{2+} and Fe^{3+} ions within the $3d^5$ configuration.[3-7] An important consequence obtained by numerical analysis is that[3]

$$a\cong F_0\zeta^4+F_1\zeta^5 , \tag{3}$$

where F_0 and F_1 are independent of the SO constant ζ.

Perturbation theories have also been available for the study of the ZFS a.[2,3,8-12] Early works include Watanabe[10] and Powell, Gabriel, and Johnston.[2] The former considered CF and SO couplings as perturbation Hamiltonians, while the latter regarded the SO interaction as the only perturbation term. As a powerful tool for investigating SO interaction processes contributing to ZFS, the perturbation procedure suggested by Macfarlane[12] and Zdansky[13] for $^4A_2(3d^3/3d^7)$ and $^3A_2(3d^2/3d^8)$ ions has been recently and successfully applied to ^6S-state ions.[3,9] The result obtained indicates a sensitive and complicated dependence on the CF parameter D_q, although an expansion of a in powers of D_q can be achieved in weak CF cases by using Watanabe's theory.[11]

Indeed, these theories are successful in accounting for experimental data of Mn^{2+} and Fe^{3+} ions in many crystals. However, as has been pointed out,[3] they fail for some cases, where other microscopic origins which play non-negligible roles in affecting ZFS must exist. These origins might be the effects of spin-spin coupling, relativistic correlated CF interaction, and covalency. The former two have been shown to be negligible.[2,14] The latter one arises from mixing between the atomic oribtals of metal and ligand ions. It is indeed important for strong covalent crystals, as will be shown in the present paper.

The present work extends previous theories to include the covalency effect by using an extended CF model. This model differs from the current CF model in that it describes the SO interaction in terms of two or more constants instead of one constant, for a $3d^n$ ion in a crystal. With the use of the extended CF model, we are able to find that in addition to the recognized origin for the ZFS parameter a of $^6S(3d^5)$ ions, namely, the CF-SO combined effect, there is another source arising from SO coupling alone. Independent of CF effect, this SO-only effect exits in crystals owing to the covalency effect which makes the SO constants different in value. Especially, it plays a most important role for tetrahedral covalent crystals.

The extended CF model will be described in Sec. II. In Sec. III we carry out extended CF-model calculations for the ZFS parameter a by means of diagonalization and perturbation to show the significance of the SO-only effect. The dependences of the ZFS parameter a on the SO constants are studied in Sec. IV, where the

0163-1829/94/49(5)/3243(10)/$06.00

Macfarlane-Zdansky procedure is adopted to analyze the SO interaction processes contributing to ZFS. The SO-only effect is investigated in more detail in Sec. V. In Sec. VI are presented satisfactory applications to Mn^{2+} ions in tetrahedral II-VI compounds and in octahedral fluoroperovskites. Conclusions are given in Sec. VII.

II. EXTENDED CRYSTAL-FIELD MODEL

As a phenomenological theory, the CF model is successful in explaining the main features of the spectroscopic properties of transition-metal ions in crystals. However, as it is limited by the assumption that the oribtals of the open $3d^n$-shell electrons are purely atomic, this model behaves crudely for understanding the fine-structure properties such as ZFS for a $3d^n$ ion in a covalent crystal. In such a case, we need to consider the mixing of atomic oribtals of metal and ligand ions in the treatment of the SO interaction which plays a main role in affecting the fine-structure properties. It is unnecessary, however, to deal with the electrostatic interaction in the same way since the fine-structure properties are insensitive to this interaction. We are thus led to an extended CF model, in which the orbital mixing is considered in the treatment of SO and CF couplings but not in the treatment of the electrostatic interaction.

The number of CF parameters remains unchanged when the CF model is extended, according to group theory. Further, the notations for the electrostatic parameters used in the CF model, usually the Racah parameters B and C as well as the Trees correction α, can be adopted in the extended CF model. Thus the difference between these two models, in a phenomenological sense, appears only in the description of the SO interaction: The extended CF model requires two or more SO parameters, depending on the symmetry under study, whereas the simple CF model takes only one parameter for any symmetry. It will be worthwhile to study the SO effects on the fine-structure properties of a transition-metal ion by taking different values for the SO parameters.

In this work we consider cubic symmetries (O, O_h, and T_d). There are two one-electron states $t_2(\xi,\eta,\zeta)$ and $e(\theta,\varepsilon)$.[15] The energy separation is denoted by $10D_q$:[15]

$$10D_q = E(e) - E(t_2) \ . \tag{4}$$

Called the cubic CF parameter, D_q is positive for O and O_h but negative for T_d. In accordance with group theory, the one-electron SO interaction involves two real parameters,[15,16] which are denoted by ζ_{tt} and ζ_{te} in the present paper (but by ζ and ζ' in Ref. 15, respectively). One parameter (ζ_{tt}) acts only within t_2 and the other (ζ_{te}) between t_2 and e.[15,16] In the case of a free ion, $\zeta_{te} = \zeta_{tt} = \zeta_{3d}$.[15,16] The CF model assumes $\zeta_{te} = \zeta_{tt} = \zeta < \zeta_{3d}$.[15]

The SO constants can be evaluated using molecular-orbital (MO) theory, where the t_2 and e oribtals are expressed as the mixtures of the oribtals of the magnetic ion and the oribtals of the ligands. Neglecting the mixing of orbitals of excited configurations, the constants can be expressed as[17]

$$\begin{aligned} \zeta_{tt} &= N_t^2(\zeta_{3d} + \tfrac{1}{2}\lambda_\pi^2 \zeta_L) \ , \\ \zeta_{te} &= N_t N_e(\zeta_{3d} - \tfrac{1}{2}\lambda_\pi \lambda_\sigma \zeta_L) \ , \end{aligned} \tag{5}$$

for an octahedral coordination, and[18,19]

$$\begin{aligned} \zeta_{tt} &= N_t^2[\zeta_{3d} + \gamma(\sqrt{2}\beta - \gamma/2)\zeta_L] \ , \\ \zeta_{te} &= N_t N_e\{\zeta_{3d} + \alpha[(1/\sqrt{6})\beta + (\sqrt{3}/6)\gamma]\zeta_L\} \ , \end{aligned} \tag{6}$$

for a tetrahedral coordination. In these expressions, λ_π, λ_σ, α, β, and γ denote covalency parameters, and ζ_{3d} and ζ_L the SO constants of metallic $3d$ and ligand p orbitals, respectively. These expressions indicate that ζ_{tt} and ζ_{te} differ from each other and from ζ_{3d}. The differences will be remarkable in the cases of strong covalency and heavy ligands having large values of ζ_L.

In the tetrahedral case, Viste and Gray[18] and Vallin and Watkins[19] have further assumed that the covalency parameters are proportional to the negative of the corresponding overlap integrals and that $N_t \approx N_e \approx 1$ to obtain the following approximate expressions:[18,19]

$$\begin{aligned} \zeta_{tt} &\approx \zeta_{3d}(1-K) \ , \\ \zeta_{te} &\approx \zeta_{3d}(1-K/8) \ , \end{aligned} \tag{7}$$

for a MnO_4 cluster, where

$$K = K_0 \zeta_L / \zeta_{3d} \ . \tag{8}$$

K_0 (>0) is a function of the covalency parameters. The results indicate that $\zeta_{tt} < \zeta_{te}$. Vallin and Watkins[19] have applied (7) to Cr^{2+} ions substituted in ZnS, CdS, ZnSe, ZnTe, and CdTe crystals. The obtained SO constants are remarkably different in value for each of the crystals. Especially, negative values of ζ_{tt} have been obtained for the latter three crystals due to the considerably large values of ζ_L of Se^{2-} and Te^{2-}. Although it is oversimplified, Eq. (7) presents a rough guide for the SO constants of Mn^{2+} ions in II-VI compounds.

Francisco and Pueyo[17] have recently carried out excellent Hartree-Fock-Roothaan calculations for the SO constants of $M = Mn^{2+}$, V^{2+}, and Cr^{z+} ($z = 1-3$) ions in octahedral MF_6 clusters. By taking into account the $3d$-orbital deformation and ligand-ligand overlaps, they have obtained the values of ζ_{tt} and ζ_{te} at different values of the metal-ligand distance R. In the case of Mn^{2+}, it has been obtained that ζ_{tt} is less than ζ_{te} by several cm^{-1}. Their results will be adopted in our calculation (Sec. VI) of the ZFS parameter a of Mn^{2+} in fluoroperovskites.

As can be seen, the covalency makes the SO constants ζ_{tt} and ζ_{te} different from each other and less than the free-ion value ζ_{3d}, for a $3d^n$ ion either in an O (or O_h) or in a T_d symmetric crystal. This property is of considerable significance in the study of the ZFS of ${}^6S(3d^5)$-state ions since the ZFS parameter a depends on the SO constants very sensitively: A small departure between ζ_{tt} and ζ_{te} will cause a great change in the value of a, as will be shown in the next section.

III. CALCULATION METHODS AND RESULTS

The calculation of the SO matrices of $3d^5$ configurations is made following Sugano, Tanabe, and Kramimura.[15] The matrices include those of $\Gamma_6(22\times22)$, $\Gamma_7(20\times20)$, and $\Gamma_8(42\times42)$ irreducible representations. They can be added directly into the CF and the electrostatic matrices published by Sugano, Tanabe, and Kramimura.[15] The obtained energy matrices enable us to calculate the ZFS parameter a of a $^6S(3d^5)$-state ion in cubic symmetry by means of either diagonalization or perturbation.

A. Diagonalization

Simultaneous diagonalization of the SO, CF, and electrostatic interactions makes it possible to obtain the value of the ZFS parameter a from the diagonalized energies of Γ_7 and Γ_8 of the ground state $^6A_1$ according to (2). To investigate the variation of a with the SO constants ζ_{tt} and ζ_{te}, we consider Mn^{2+} ions in a tetrahedral coordination having parameters values $B=405$, $C=3437$, $\alpha=0$, and $D_q=-575.2$ (in cm^{-1}), which are just those found for Mn^{2+}:ZnS.[20] The obtained results are listed in Table I. They are compared to the following results of the CF model ($\zeta=\zeta_{tt}=\zeta_{te}$): $a=2.7\times10^{-4}$ cm^{-1} for $\zeta=\zeta_{3d}=333$ cm^{-1}, $a=1.6\times10^{-4}$ cm^{-1} for $\zeta=300$ cm^{-1}, $a=1.2\times10^{-4}$ cm^{-1} for $\zeta=270$ cm^{-1}, and $a=0$ for $\zeta=0$. More examples showing the dependences of a on ζ_{te} and ζ_{tt} are plotted in Figs. 1 and 2. The variation of a of Mn^{2+} ions with the CF parameter D_q for given values of the SO constants ζ_{te} and ζ_{tt} is calculated by assuming $B=830$, $C=3122$,and $\alpha=76$, in cm^{-1}, as given in Table II and Fig. 3.

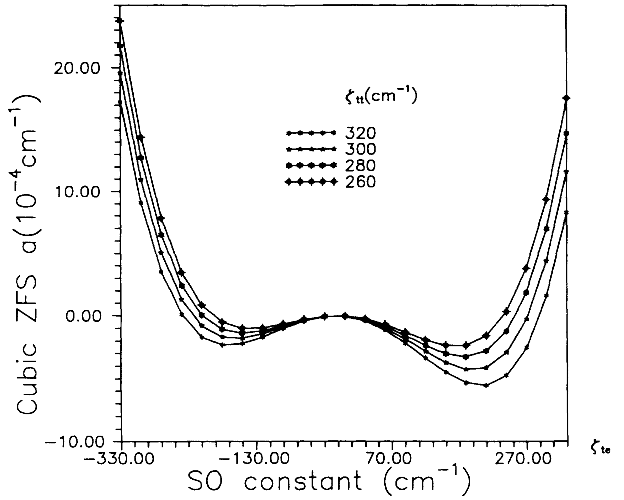

FIG. 1. Zero-field splitting parameter a of Mn^{2+} ions as a function of ζ_{te}, calculated by assuming $B=822$ cm^{-1}, $C=3122$ cm^{-1}, $\alpha=76$ cm^{-1}, and $D_q=800$ cm^{-1}.

B. Perturbation

Since the SO coupling is considerably weak compared to the electrostatic and CF interactions, it is reasonable to regard the SO coupling as the perturbation to the other two interactions in the perturbation approach of a. In such an approach, the first- to third-order perturbations have no contributions because of the rank-4 ZFS nature of a. Equation (2) is applicable to every perturbation order:

$$a^{(\lambda)}=[E^{(\lambda)}(\Gamma_8)-E^{(\lambda)}(\Gamma_7)]/3\ , \tag{9}$$

TABLE I. Zero-field splitting parameter a (in units of 10^{-4} cm^{-1}) of Mn^{2+} as a function of the SO constants ζ_{te} and ζ_{tt}, evaluated assuming $B=405$, $C=3437$, $\alpha=0$, and $D_q=-575.2$ cm^{-1}.

	$\zeta_{te}=270$ cm^{-1}					$\zeta_{tt}=270$ cm^{-1}			
ζ_{tt}		Perturbation			ζ_{te}		Perturbation		
(cm^{-1})	Diagonalization	$a^{(4)}$	$a^{(5)}$	Total	(cm^{-1})	Diagonalization	$a^{(4)}$	$a^{(5)}$	Total
330	−7.0	−6.7	−0.3	−7.0	330	14.9	15.6	−0.8	14.8
300	−2.7	−2.3	−0.3	−2.6	300	6.7	7.2	−0.5	6.7
270	1.2	1.6	−0.3	1.3	270	1.2	1.6	−0.3	1.3
240	4.7	5.0	−0.3	4.7	240	−2.0	−1.8	−0.2	−2.0
210	7.8	8.1	−0.3	7.8	210	−3.5	−3.4	−0.1	−3.5
180	10.5	10.7	−0.2	10.5	180	−3.9	−3.8	−0.0	−3.8
150	12.8	13.0	−0.2	12.8	150	−3.5	−3.4	−0.0	−3.4
90	16.1	16.3	−0.1	16.2	90	−1.7	−1.7	0.0	−1.7
0	18.3	18.3	−0.0	18.3	0	−0.0	−0.0	0.0	−0.0
−90	17.1	17.0	0.1	17.1	−90	−1.2	−1.2	0.0	−1.2
−150	14.4	14.3	0.1	14.4	−150	−2.4	−2.4	0.0	−2.4
−180	12.7	12.5	0.2	12.7	−180	−2.4	−2.4	−0.0	−2.4
−210	10.5	10.3	0.2	10.5	−210	−1.5	−1.4	−0.1	−1.5
−240	8.0	7.8	0.2	8.0	−240	0.7	0.8	−0.1	−0.7
−270	5.1	4.9	0.2	5.1	−270	4.7	4.9	−0.2	4.7
−300	2.0	1.7	0.2	1.9	−300	11.1	11.4	−0.4	11.0
−330	−1.5	−1.8	0.3	−1.5	−330	20.5	21.0	−0.4	20.6

TABLE II. Zero-field splitting parameter a (in units of 10^{-4} cm^{-1}) of Mn^{2+} as a function of the crystal-field parameter D_q, calculated assuming $B=830$, $C=3122$, and $\alpha=76$ cm^{-1}.

D_q	$\zeta_{te}=330$ cm^{-1}, $\zeta_{tt}=300$ cm^{-1}				$\zeta_{te}=\zeta_{tt}=315$ cm^{-1}			
		Perturbation				Perturbation		
(cm^{-1})	Diagonalization	$a^{(4)}$	$a^{(5)}$	Total	Diagonalization	$a^{(4)}$	$a^{(5)}$	Total
1800	256.5	216.8	38.7	255.5	206.0	171.6	33.5	205.1
1600	101.9	89.4	12.4	101.8	77.7	66.9	10.7	77.6
1400	50.7	45.2	5.5	50.6	36.1	31.3	4.7	36.0
1200	28.6	25.6	2.9	28.5	18.5	16.0	2.4	18.4
1000	17.5	15.8	1.7	17.5	9.9	8.5	1.4	9.9
800	11.5	10.5	1.0	11.5	5.3	4.4	0.9	5.3
600	8.0	7.4	0.6	8.0	2.7	2.1	0.5	2.6
400	5.9	5.6	0.3	5.9	1.2	0.9	0.3	1.2
200	4.8	4.6	0.2	4.8	0.4	0.3	0.1	0.4
0	4.4	4.4	0.0	4.4	0	0	0	0
−200	4.5	4.6	−0.2	4.4	0.1	0.2	−0.1	0.1
−400	5.2	5.6	−0.3	5.3	0.6	0.9	−0.3	0.6
−600	6.7	7.4	−0.6	6.8	1.7	2.1	−0.5	1.6
−800	9.4	10.5	−1.0	9.5	3.6	4.4	−0.9	3.5
−1000	14.2	15.8	−1.7	14.1	7.1	8.5	−1.4	7.1
−1200	22.8	25.6	−2.9	22.7	13.6	16.0	−2.4	13.6
−1400	39.7	45.2	−5.5	39.7	26.7	31.3	−4.7	26.6
−1600	77.1	89.4	−12.4	77.0	56.3	66.9	−10.7	56.2
−1800	179.0	216.8	−38.7	178.1	139.0	171.6	−33.5	138.1

where $E^{(\lambda)}(\Gamma_7)$ and $E^{(\lambda)}(\Gamma_8)$ denote the λth-order energies of Γ_7 and Γ_8 of $^6A_1$. The present calculations are carried out to fifth order and by taking into account all states in the $3d^5$ configuration. The results obtained are displayed in Tables I and II for comparison with those evaluated by means of diagonalization. It is seen that

$$a \cong a^{(4)} + a^{(5)} . \tag{10}$$

C. Discussions

It is obvious that $a^{(4)}$ is proportional to the fourth power of the SO constant ζ in the CF model. Similarly, $a^{(5)} \propto \zeta^5$. Thus Eqs. (3) and (10) are actually equivalent, and we obtain

$$F_0 = a^{(4)}/\zeta^4 , \quad F_1 = a^{(5)}/\zeta^5 . \tag{11}$$

It is seen from Table II that $a^{(4)}$ is an even function of D_q and that $a^{(5)}$ is an odd function:

$$a^{(4)}(D_q) = a^{(4)}(-D_q) , \quad a^{(5)}(D_q) = -a^{(5)}(-D_q) , \tag{12}$$

as has been mentioned previously.[3,8] As a result of this

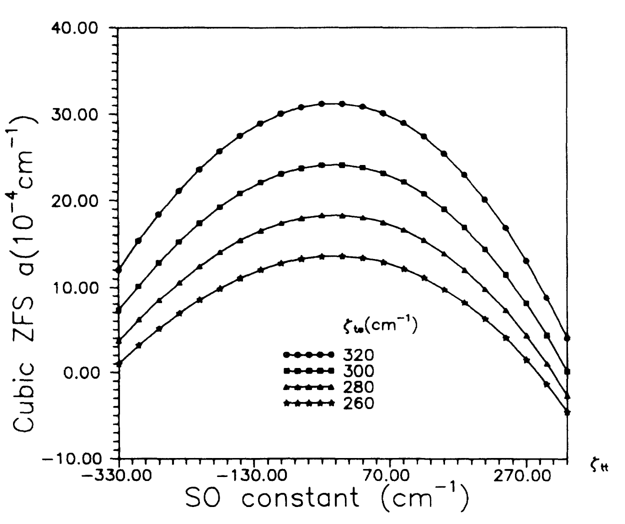

FIG. 2. Zero-field splitting parameter a of Mn^{2+} ions as a function of ζ_{tt}, calculated by assuming $B=830$ cm^{-1}, $C=3122$ cm^{-1}, $\alpha=76$ cm^{-1}, and $D_q=800$ cm^{-1}.

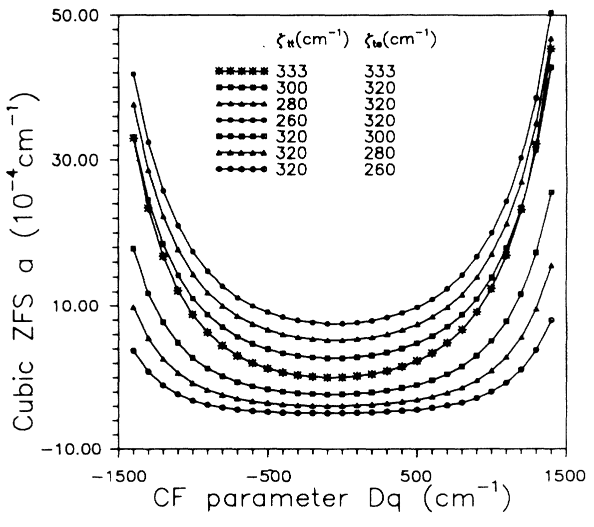

FIG. 3. Zero-field splitting parameter a of Mn^{2+} ions as a function of D_q, calculated by assuming $B=822$ cm^{-1}, $C=3122$ cm^{-1}, and $\alpha=76$ cm^{-1}.

and the fact that $a^{(4)}(|D_q|)>0$ and $a^{(5)}(|D_q|)>0$, we obtain

$$a(|D_q|)>a(-|D_q|)\ . \tag{13}$$

These properties are ascribed to the self-complimentary nature of the d^5 configuration:[3,8] A d^5-electron configuration ion can be regarded equivalently as a five-d-hole configuration. This requires the ZFS parameters of a d^5 ion to remain unchanged when inverting signs of both the CF and SO parameters.

It is noted that in the CF model, the SO constant ζ is assumed to be positive and less than the free-ion value ζ_{3d}, which has been calculated to be 333 cm^{-1} for Mn^{2+}.[21] Thus, according to the CF model, the value of a for a given crystal should be positive[22] and less than $a(\zeta_{3d})$, where $a(\zeta_{3d})$, called the CF-model limitation value, is the value evaluated by taking $\zeta=\zeta_{3d}$. In other words, if a has been observed to be in the range $0<a<a(\zeta_{3d})$, the CF model is capable of accounting for it by assuming $0<\zeta<\zeta_{3d}$; otherwise, it must be unsuccessful. An example of success is Mn^{2+}:KZnF_3, for which $B=830$, $C=3122$, $\alpha=76$, and $D_q=822$ (in cm^{-1}) have been reported.[23] By diagonalization, the CF-model limitation value $a(\zeta_{3d})$ is calculated to be 7.0×10^{-4} cm^{-1}, greater than the experimental value $a=(6.3\pm0.1)\times10^{-4}$ cm^{-1}.[24] Thus we are able to account for the observed value by taking $\zeta=324$ cm^{-1}.[8] The Mn^{2+}:ZnS crystals serve as an opposite example: $a(\zeta_{3d})=2.7\times10^{-4}$ cm^{-1}, less than the observed value 7.9×10^{-4} cm^{-1}.[25] Thus the CF model cannot be successful for this crystal unless one unreasonably takes ζ greater than ζ_{3d}.

One of the important consequences of the extended CF model appears that the value of a can be significantly greater than the CF-model limitation value $a(\zeta_{3d})$. This usually happens when $\zeta_{tt}<\zeta_{te}$, as can be seen from Table I and Fig. 2. For a given value of ζ_{te}, a increases remarkably with decreasing ζ_{tt} and reaches a maximum at ζ_{tt} close to zero. The maximum value can be one order of magnitude greater than the CF-model limitation value $a(\zeta_{3d})$, which equals 2.7×10^{-4} cm^{-1} for the parameter values used in the calculation of Table I and 7.2×10^{-4} cm^{-1} in Fig. 2. Another important consequence of the extended CF model is that the values of a can be negative in crystals where $\zeta_{tt}>\zeta_{te}$. Although indeed a is usually positive, some negative values of a have been reported as well, for example, in Mn^{2+}:CaWO_4 [$a=(-6.9\pm0.2)\times10^{-4}$ cm^{-1} (Ref. 26)] and in Mn^{2+}:SrWO_4 [$a=-(3.1\pm0.2)\times10^{-4}$ cm^{-1} (Ref. 27)]. The extended CF model provides a possible way to explain negative values of a, for which the CF model can never account. These consequences show the usefulness of the extended CF model in the study of the ZFS of $^6S(3d^5)$-state ions.

The interesting thing appearing in Table II and Fig. 3 is that a does not vanish at vanishing D_q when $\zeta_{tt}\neq\zeta_{te}$. Obviously, this value cannot be ascribed to the CF-SO combined effect since it exits at $D_q=0$. Instead, it has to be ascribed to the SO interaction alone.

This SO-only effect arises because of the difference between the SO constants. It exists in crystals since the SO constants differ from each other due to the covalency effect. Therefore the SO-only effect is actually one of results of the covalency effect in affecting ZFS.

The contribution of the SO-only effect is denoted by a_{SO}, while that of the CF-SO combined effect by $a_{\text{CF}-\text{SO}}$, so that we obtain

$$a=a_{\text{CF}-\text{SO}}+a_{\text{SO}}\ , \tag{14}$$

where

$$a_{\text{SO}}=a(D_q=0)\ . \tag{15}$$

Since $a_{\text{SO}}=0$ when $\zeta_{tt}=\zeta_{te}$, the SO-only effect cannot be taken into account by using the CF model. The SO-only effect will be discussed in more detail in Sec. V after an investigation of the dependences of a on the SO constants presented in the next section.

IV. DEPENDENCES ON THE SPIN-ORBIT CONSTANTS

As shown in Table I and Figs. 1 and 2, the ZFS parameter a depends on the SO constants ζ_{te} and ζ_{tt} in quite different ways. Considering the difference between values of the SO constants, Eq. (3) does not work. However, perturbation calculations enable us to obtain an analytical expression of a in powers of ζ_{te} and ζ_{tt} for given values of B, C, α, and D_q. To achieve this we write the λth-order ($\lambda=4,5,\ldots$) contribution as

$$a^{(\lambda)}=\sum_{n=0}^{\lambda} f_n^{(\lambda)}\zeta_{te}^{\lambda-n}\zeta_{tt}^{n}\ . \tag{16}$$

Independent of ζ_{te} and ζ_{tt}, the coefficients $f_n^{(\lambda)}$ ($\lambda=4$ and 5) are related to F_0 and F_1 defined in (3) by the equations $F_0=\sum_n f_n^{(4)}$ and $F_1=\sum_n f_n^{(5)}$.

The values of $f_n^{(\lambda)}$ can be obtained by numerical analysis. Take a Mn^{2+}:ZnS crystal as an illustration, where $B=405$, $C=3437$, $\alpha=0$, and $D_q=-575.2$, in cm^{-1}, have been reported.[20] The fifth and higher orders are negligible for this value of D_q. We obtain

$$a\approx[3.44\zeta_{te}^4-2.83\zeta_{te}^2\zeta_{tt}^2-0.187(\zeta_{te}\zeta_{tt}^3+\zeta_{te}^3\zeta_{tt})]\times10^{-13}(\text{cm}^{-1})^{-3}\ . \tag{17}$$

As illustrated in (17) and as general rules, we find the following relations for the coefficients $f_n^{(4)}$:

$$\begin{aligned} &f_0^{(4)}>-f_2^{(4)}\gg-f_1^{(4)}\approx-f_3^{(4)}\gg-f_4^{(4)}>0\ ,\\ &f_0^{(4)}>-(f_2^{(4)}+f_1^{(4)}+f_3^{(4)}+f_4^{(4)})\ ,\\ &f_4^{(4)}\approx0\ . \end{aligned} \tag{18}$$

These show that the fourth-order contribution is composed of two parts, one being positive and proportional to ζ_{te}^4 and the other negative and in powers of ζ_{tt}. A similar case occurs at fifth order and also for the total value of a. The ZFS parameter a is therefore determined by the relative magnitudes of these two parts. In particular, it is positive when $\zeta_{te}=\zeta_{tt}$. However, a small departure between values of ζ_{te} and ζ_{tt} will cause a great change in the value of a, as shown in Table I and Figs. 1 and 2.

TABLE III. Expressions of E_i.

$E_1 = 10B + 6C + 12\alpha - 10D_q$	$E_9 = 27B + 9C + 18\alpha + 10D_q$
$E_2 = 19B + 7C + 10\alpha$	$E_{10} = 15B + 10C + 22\alpha + 20D_q$
$E_3 = 10B + 6C + 12\alpha + 10D_q$	$E_{11} = 31B + 12C + 14\alpha - 10D_q$
$E_4 = 15B + 10C + 22\alpha - 20D_q$	$E_{12} = 22B + 9C + 20\alpha - 10D_q$
$E_5 = 27B + 9C + 18\alpha - 10D_q$	$E_{13} = 19B + 8C + 26\alpha$
$E_6 = 17B + 9C + 22\alpha - 10D_q$	$E_{14} = 23B + 8C + 18\alpha$
$E_7 = 37B + 12C + 14\alpha$	$E_{15} = 31B + 12C + 14\alpha + 10D_q$
$E_8 = 17B + 9C + 22\alpha + 10D_q$	$E_{16} = 22B + 9C + 20\alpha + 10D_q$

The different dependences on the SO constants ζ_{te} and ζ_{tt} is understandable from the SO coupling processes contributing to ZFS. Let us analyze these fourth-order processes. The ground state ${}^6A_1$ has a configuration $t_2^3e^2$ and it couples only with the ${}^4T_1$ states, including ${}^4T_1(t_2^4e)$, ${}^4T_1(t_2^3e^2)$, and ${}^4T_1(t_2^2e^3)$. Accordingly, the perturbation processes can be denoted as

$$ {}^6A_1 \xrightarrow{\mathcal{H}_{\rm SO}} {}^4T_1 \xrightarrow{\mathcal{H}_{\rm SO}} n \xrightarrow{\mathcal{H}_{\rm SO}} {}^4T_1 \xrightarrow{\mathcal{H}_{\rm SO}} {}^6A_1 \ , \tag{19}$$

where n refers to the excited states and ${}^4T_1$ the mixture of ${}^4T_1(t_2^4e)$, ${}^4T_1(t_2^3e^2)$, and ${}^4T_1(t_2^2e^3)$. As a rough guide and for simplicity, we neglect the mixing of all states to regard, for example, ${}^4T_1$ as an individual of ${}^4T_1(t_2^4e)$, ${}^4T_1(t_2^3e^2)$, and ${}^4T_1(t_2^2e^3)$. The neglect is actually equivalent to the Macfarlane-Zdansky procedure: The CF and diagonal parts of electrostatic interaction are regarded as the unperturbed Hamiltonian and the SO and off-diagonal parts of electrostatic interaction as the perturbations. Since the SO interaction between states of different configurations $t_2^me^{5-m}$ is proportional to ζ_{te},[15] only the processes in which the SO couplings are all between different configurations make a contribution proportional to ζ_{te}^4. Other processes will contribute values proportional to $\zeta_{te}^{4-m}\zeta_{tt}^m (m=1-4)$. Detailed calculations enable us to obtain

$$\begin{aligned} f_0^{(4)} &= \frac{6}{5}\left[\frac{1}{E_1^2E_4}+\frac{1}{E_3^2E_{10}}\right] \\ &\quad + \frac{1}{10}\left[\frac{1}{E_1}+\frac{1}{E_3}\right]^2\left[\frac{2}{E_{14}}+\frac{3}{E_7}-\frac{1}{E_{13}}\right] , \\ f_2^{(4)} &= -\frac{1}{20}\left[\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2\left[\frac{8}{E_{11}}+\frac{2}{E_{12}}-\frac{1}{E_5}-\frac{1}{E_6}\right]\right. \\ &\qquad + \left[\frac{1}{E_2}+\frac{1}{E_3}\right]^2 \\ &\qquad \left.\times\left[\frac{8}{E_{15}}+\frac{2}{E_{16}}-\frac{1}{E_8}-\frac{1}{E_9}\right]\right] , \\ f_1^{(4)} &= f_3^{(4)} = f_4^{(4)} = 0 \ , \end{aligned} \tag{20}$$

where E_i denote the energy differences between the exited and ground states as have been listed in Table III. Equation (20) shows a positive $f_0^{(4)}$ and a negative $f_2^{(4)}$. Further, the relation $f_0^{(4)} > |f_2^{(4)}|$ holds, not only because of the greater numerical coefficients, but also because smaller energies appeared in the expression of $f_0^{(4)}$. [Please note that E_1 (E_3) and E_4 (E_{10}) are lowest states of the spin quartets and spin doublets, respectively, for a ${}^6S(3d^5)$ in octahedral (tetrahedral) coordination.] Finally, there are no contributions to $f_1^{(4)}$, $f_3^{(4)}$, and $f_4^{(4)}$ for our adopted approximation. They should arise from higher orders, and thus they must be considerably small in magnitude compared to $f_2^{(4)}$. These points are consistent with (18). Application to Mn^{2+}:ZnS gives $f_0^{(4)}=1.2$ and $f_2^{(4)}=-0.9$ as rough values to be compared to $f_0^{(4)}=3.44$ and $f_2^{(4)}=-2.83$, all in 10^{-13} $(\mathrm{cm}^{-1})^{-3}$, given in (17). The above analysis shows that the different dependences of a on the SO constants occur because of different SO interaction processes, different values of the SO interaction between states, and different energies of inherent excited states. The three ${}^4T_1$ states are crucial in affecting ZFS as they are the only states that couple with the ground state ${}^6A_1$. Apart from these states, the ${}^2T_2$ and ${}^2E$ states play important roles. Other states, including ${}^4A_1$, ${}^4A_2$, ${}^4T_2$, ${}^4E$, ${}^2A_1$, ${}^2A_2$, and ${}^2T_1$, contribute negligibly.

V. SO-ONLY EFFECT

The SO-only effect has been noted in Sec. III such that a will be nonzero at $D_q=0$ if $\zeta_{te}\neq\zeta_{tt}$. This effect is understandable from group theory: If $\zeta_{te}=\zeta_{tt}$ and $D_q=0$, the system has full rotational symmetry and a is zero, since Γ_7 and Γ_8 belong jointly to the irreducible representation $D_{5/2}$. If either of these conditions is not satisfied, the effective symmetry reduce to O_h (or O,T_d), and Γ_7 and Γ_8 can be expected to separate. In other words, the SO-only effect must exist in crystals.

The contribution of the SO-only effect can be separated from that of the CF-SO combined effect. In the case of $B=405$, $C=3437$, $\alpha=0$, and $D_q\in[-600,-300]$, in cm^{-1}, we obtain

$$a_{\rm SO} \approx \zeta_{te}(\zeta_{te}-\zeta_{tt})(2.82\zeta_{te}^2+2.665\zeta_{te}\zeta_{tt}+0.155\zeta_{tt}^2) \ , \tag{21}$$

$$\begin{aligned} a_{\rm CF-SO} \approx \{ & 1.04|D_q|^{2.09}\zeta_{te}^4 - 0.628|D_q|^{2.07}\zeta_{te}^2\zeta_{tt}^2 \\ & -4.08|D_q|^{1.41}(\zeta_{te}^3\zeta_{tt}+\zeta_{te}\zeta_{tt}^3)\}\times 10^{-6} \ , \end{aligned} \tag{22}$$

in units of 10^{-13} $(\mathrm{cm}^{-1})^{-3}$, where D_q is in units of cm^{-1}. The results are useful in the study of the ZFS of Mn^{2+} ions in II-VI compounds (see Sec. VI).

Equation (21) indicates a $\zeta_{te}-\zeta_{tt}$ dependence of $a_{\rm SO}$:

$a_{\rm SO}$ is positive when $\zeta_{te} > \zeta_{tt}$, negative when $\zeta_{te} < \zeta_{tt}$, and zero when $\zeta_{te} = \zeta_{tt}$. The SO-only effect plays an important role for crystals having weak CF potentials and quite different values of ζ_{te} and ζ_{tt}. To see this, we assume $\zeta_{tt} = 0$ and $\zeta_{te} = 300$ cm^{-1} and obtain $a_{\rm SO} = 22.8 \times 10^{-4}$ cm^{-1} and $a_{\rm CF\text{-}SO} = 1.3 \times 10^{-4}$ cm^{-1} for $D_q = -300$ cm^{-1} from (21) and (22). Other examples have been given in Table II, where $a_{\rm SO} = 4.4 \times 10^{-4}$ cm^{-1} is shown, compared to $a_{\rm CF\text{-}SO} = 0.4 \times 10^{-4}$ cm^{-1} for $D_q = 200$ cm^{-1}, 1.5×10^{-4} cm^{-1} for $D_q = 400$ cm^{-1}, and 7.1×10^{-4} cm^{-1} for $D_q = 800$ cm^{-1}. Table II shows that the SO-only effect is negligible for strong CF potentials. It is negligible too for highly ionic crystals where $\zeta_{te} \approx \zeta_{tt}$.

An approximate expression can be derived for the SO-only effect by using the Macfarlane-Zdansky perturbation procedure. We obtain, from (15), (16), and (20),

$$a_{\rm SO} \approx \frac{2}{5D_1^2}\left[\frac{6}{D_4}+\frac{2}{D_{14}}+\frac{3}{D_7}-\frac{1}{D_{13}}\right]\zeta_{te}^4 - \frac{1}{10}\left[\frac{1}{D_1}+\frac{1}{D_2}\right]^2\left[\frac{8}{D_{11}}+\frac{2}{D_{12}}-\frac{1}{D_5}-\frac{1}{D_6}\right]\zeta_{te}^2\zeta_{tt}^2 , \qquad (23)$$

where $D_i = E_i(D_q = 0)$ with E_i being given in Table III. Equation (23) does not strictly satisfy the condition $a_{\rm SO}(\zeta_{te} = \zeta_{tt}) = 0$ owing to neglect of the mixing of states.

VI. APPLICATIONS

In this section, we apply the theory presented in the preceding sections to Mn^{2+} ions doped in the II-VI compounds ZnS, ZnSe, ZnTe, and CdTe and in fluoroperovskites $\mathrm{KMgF_3}$, $\mathrm{RbCdF_3}$, and $\mathrm{KZnF_3}$. These crystals provide typical examples of strong, intermediate, and weak SO-only effects, allowing us to understand more about the ZFS parameter a of $^6S(3d^5)$-state ions.

A. Mn^{2+} ions in tetrahedral II-VI compounds

It has been experimentally observed that $B = 405$, $C = 3437$, $\alpha = 0$, and $D_q = -575.2$ for Mn^{2+}:ZnS (Ref. 20) and $B = 750$, $C = 2760$, $\alpha = 0$, and $D_q = -372$ for Mn^{2+}:ZnSe,[28] in units of cm^{-1}. The free-ion SO constant ζ_{3d} of Mn^{2+} has been calculated to be 333 cm^{-1} by Blume and Watson.[21] Accordingly, the CF-model limitation value $a(\zeta_{3d})$ is evaluated to be 2.8×10^{-4} cm^{-1} for Mn^{2+}:ZnS and 1.4×10^{-4} cm^{-1} for Mn^{2+}:ZnSe. These values are considerably less than the experimental results 7.9×10^{-4} cm^{-1} for Mn^{2+}:ZnS and 19.7×10^{-4} cm^{-1} for Mn^{2+}:ZnSe, respectively. This indicates that the CF model must be unsuccessful in these crystals, for this model takes $\zeta = \zeta_{te} = \zeta_{tt} < \zeta_{3d}$. In Table IV are listed the results calculated in the CF model and by assuming $\zeta = 300$ cm^{-1} for ZnS, 280 cm^{-1} for ZnSe, and 260 cm^{-1} for ZnTe and CdTe. In the calculations we have assumed that Mn^{2+}:ZnTe and Mn^{2+}:CdTe have a D_q value of -300 cm^{-1} and values of B, C, and α identical to those of Mn^{2+}:ZnSe, without altering the final conclusion that the CF model is incapable of accounting for the experimental values of the ZFS parameter a of Mn^{2+} ions in these four compounds.

Since

$$|D_q(\mathrm{Mn}^{2+}\text{:ZnS})| > |D_q(\mathrm{Mn}^{2+}\text{:ZnSe})| > |D_q(\mathrm{Mn}^{2+}\text{:ZnTe})| ,$$

it will be expected that

$$a(\mathrm{Mn}^{2+}\text{:ZnS}) > a(\mathrm{Mn}^{2+}\text{:ZnSe}) > a(\mathrm{Mn}^{2+}\text{:ZnTe})$$

if the CF-SO combined effect can play a predominant role. However, the experiments show an opposite order:

$$a(\mathrm{Mn}^{2+}\text{:ZnS}) < a(\mathrm{Mn}^{2+}\text{:ZnSe}) < a(\mathrm{Mn}^{2+}\text{:ZnTe}) . \qquad (24)$$

($a = 7.9$ for Mn^{2+}:ZnS,[25] 19.7 for Mn^{2+}:ZnSe,[29] 29.6 for Mn^{2+}:ZnTe,[30] and 27 for Mn^{2+}:CdTe,[29] in units of 10^{-4} cm^{-1}.) This indicates the importance of the SO-only effect in these crystals.

In order to interpret (24), let us first adopt Eqs. (7) and

TABLE IV. Zero-field splitting parameter a (in units of 10^{-4} cm^{-1}) of Mn^{2+} ions in tetrahedral II-VI crystals. The first and the third rows list results calculated by means of diagonalization and the second row by using Eqs. (21) and (22).

	ζ_{te}	ζ_{tt}	$a_{\rm SO}$	$a_{\rm CF\text{-}SO}$	a	a (expt.)
ZnS	329.5	304.7	4.8	3.1	7.9	7.9[a]
	329.5	304.7	4.8	3.3	8.1	
	300	300	0	1.8	1.8	
ZnSe	317.4	207.8	17.8	2.0	19.8	19.7[b]
	317.4	207.8	16.2	1.8	18.0	
	280	280	0	0.7	0.7	
ZnTe	294.7	26.6	23.4	1.4	24.8	29.6[c]
(CdTe)	294.7	26.6	21.0	1.2	22.3	(27[b])
	260	260	0	0.3	0.3	

[a] Reference 25.

[b] Reference 29.

[c] Reference 30.

(8) given by Viste and Gray[18] and Vallin and Watkins[19] to estimate the values of the SO constants ζ_{te} and ζ_{tt}. Used in our calculations are $K_0=0.0741$ for all the three ligands and the theoretical values $\zeta^L=382.4$ cm^{-1} for S^{2-}, 1689 cm^{-1} for Se^{2-}, and 4136 cm^{-1} for Te^{2-} reported by Barnes and Smith.[31] Since ζ^L varies so rapidly between S^{2-}, Se^{2-}, and Te^{2-}, any variation in K_0 is of little further consequence on the values of ζ_{te} and ζ_{tt}. The results obtained are as given in Table IV. As can be seen, $\zeta_{te}>\zeta_{tt}>0$ in each case; the difference between ζ_{te} and ζ_{tt} depends on the ligand and it is 25 cm^{-1} for S^{2-}, 110 cm^{-1} for Se^{2-}, and 268 cm^{-1} for Te^{2-}. The contribution of the SO-only effect, $a_{\rm SO}$, is then calculated by means of diagonalization to be 4.8×10^{-4} cm^{-1} for Mn^{2+}:ZnS, 17.2×10^{-4} cm^{-1} for Mn^{2+}:ZnSe, and 23.4×10^{-4} cm^{-1} for Mn^{2+}:ZnTe and Mn^{2+}:CdTe. The results show that

$$a_{\rm SO}({\rm Mn}^{2+}{:}{\rm ZnS})<a_{\rm SO}({\rm Mn}^{2+}{:}{\rm ZnSe})<a_{\rm SO}({\rm Mn}^{2+}{:}{\rm ZnTe})\ . \tag{25}$$

On the other hand, the contribution of the CF-SO combined effect is found to be $a_{\rm CF\text{-}SO}=3.1\times10^{-4}$ cm^{-1} for Mn^{2+}:ZnS, 2.0×10^{-4} cm^{-1} for Mn^{2+}:ZnSe, and 1.4×10^{-4} cm^{-1} for Mn^{2+}:ZnTe and Mn^{2+}:CdTe. The order of magnitude of $a_{\rm CF\text{-}SO}$ appears to be opposite to (25):

$$a_{\rm CF\text{-}SO}({\rm Mn}^{2+}{:}{\rm ZnS})>a_{\rm CF\text{-}SO}({\rm Mn}^{2+}{:}{\rm ZnSe})>a_{\rm CF\text{-}SO}({\rm Mn}^{2+}{:}{\rm ZnTe})\ . \tag{26}$$

It is seen that in each of the crystals, both $a_{\rm CF\text{-}SO}$ and $a_{\rm SO}$ are positive. Further, $a_{\rm SO}$ is greater than $a_{\rm CF\text{-}SO}$ in each case. Especially, it is one order of magnitude larger in the cases of Mn^{2+}:ZnSe, Mn^{2+}:ZnTe, and Mn^{2+}:CdTe. Therefore the total contribution $a=a_{\rm SO}+a_{\rm CF\text{-}SO}$ is predominated by $a_{\rm SO}$, and thus we obtain an order given by (24) as the experiments have indicated.

It is important to note that because of the large differences between the SO constants, the contribution $a_{\rm CF\text{-}SO}$ of the CF-SO combined effect (as has been listed in Table IV) is considerably greater than the CF-model limitation value $a(\zeta_{3d})$ (which equals 2.8 for Mn^{2+}:ZnS, 1.4 for Mn^{2+}:ZnSe, and 0.8 for Mn^{2+}:ZnTe and Mn^{2+}:CdTe, in 10^{-4} cm^{-1}) in each of the cases. This implies that the CF model cannot account even for the CF-SO combined effect for these crystals unless one unreasonably takes a SO constant ζ which is greater than the free-ion value ζ_{3d}. Another interesting point is that the CF-SO combined effect contributes a value which is so small that one can simply assume $D_q=0$ in the calculation in the cases of Mn^{2+}:ZnSe, Mn^{2+}:ZnTe, and Mn^{2+}:CdTe.

The values of $a_{\rm SO}$ and $a_{\rm CF\text{-}SO}$ calculated by means of diagonalization are shown in Table IV. Also listed in the table are results evaluated by using Eqs. (21) and (22), which have been derived for $B=405$, $C=3437$, $\alpha=0$, and $D_q\in[-600,-300]$, in cm^{-1}. Consistence between these results indicates the usefulness of these approximate equations. As is expected, it works indeed very well for Mn^{2+}:ZnS where the values of B, C, and α are just those used in the derivation of these equations. It works satisfactorily as well for the other three crystals where the parameters B, C, and α are remarkably different from those of Mn^{2+}:ZnS. It does so because the ZFS parameter a depends on the SO constants so rapidly that variations in these electrostatic parameters are of little consequence.

The above calculations have indicated that the CF model can never account for the experimental data of a of Mn^{2+} ions in ZnS, ZnSe, ZnTe, and CdTe crystals because of the important SO-only effect. Zhou, Zhao, and Ning[7] have recently tried to use the CF model to explain the ZFS parameter a of Mn^{2+}:ZnS. They have assumed a positive D_q value of $+600$ cm^{-1} as well as $\zeta=343$ cm^{-1}, which is greater than the free-ion value $\zeta_{3d}=333$ cm^{-1} calculated by Blume and Watson.[21] The obtained results $a=7.84\times10^{-4}$ cm^{-1} agree with the experimental value 7.9×10^{-4} cm^{-1}.[25] As a positive value of D_q arises from an octahedral coordination, the authors had to assume octahedral sites for the Mn^{2+} ions in ZnS crystals. However, it has been widely accepted that the Mn^{2+} ions in ZnS, ZnSe, CdTe, and ZnTe crystals are located tetrahedrally and substitutionally as other iron-group ions such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Cr^{2+} do in these as well as other tetrahedrally coordinated semiconductors (see the review article Ref. 32 and references therein.

B. Mn^{2+} ions in fluoroperovskites

By using the CF model, Yu and Rudowicz[8] have recently calculated the ZFS of Mn^{2+} ions in fluoroperovskites, including KMgF$_3$, KZnF$_3$, and RbCdF$_3$. The results obtained are in good agreement with the observed values. In the present section, we show that the SO-only effect is of a little importance in these crystals.

The SO constants ζ_{te} and ζ_{tt} depend on overlap integrals, and thus they are functions of the distance R between the magnetic ion and the ligands. The values of $R({\rm Mn}^{2+}-{\rm F}^-)$ in fluoroperovskites doped with Mn^{2+} impurities have been determined by Barriuso and Moreno[33] from the experimental values of superhyperfine constant. These enable us to obtain ζ_{te} and ζ_{tt} in accordance with Francisco and Pueyo.[17] The result, as given in Table V, are compared to the free-ion value $\zeta_{3d}=333$ cm^{-1} and $\zeta=324$ cm^{-1} adopted in Yu and Rudowicz's calculations.

The electrostatic and CF parameters have been experimentally determined from optical spectra to be $B=830$, $C=3122$, $\alpha=76$, and $D_q=822$ for Mn^{2+}:KZnF$_3$,[23] $B=847$, $C=3086$, $\alpha=65$, and $D_q=844$ for Mn^{2+}:KMgF$_3$,[34] and $B=825$, $C=3136$, $\alpha=76$, and $D_q=715$ for Mn^{2+}:RbCdF$_3$,[23] in units of cm^{-1}. By using these parameter values, the CF-model limitation value $a(\zeta_{3d})$ is calculated to be 7.2 for Mn^{2+}:KZnF$_3$, 8.0 for Mn^{2+}:KMgF$_3$, and 5.0 for Mn^{2+}:RbCdF$_3$, in 10^{-4} cm^{-1}. They are greater than the experimental values

TABLE V. Zero-field splitting parameter a of Mn^{2+} ions in fluoroperovskites. ζ_{te} and ζ_{tt} are given in cm^{-1}, R in Å, and a in 10^{-4} cm^{-1}.

	R	ζ_{te}	ζ_{tt}	a_{SO}	$a_{CF\text{-}SO}$	a	a (expt.)
$KZnF_3$	2.084(11)	314.1(1)	308.6(3)	0.8(1)	5.7(1)	6.5(1)	6.3(1)[a]
		324	324	0	6.4	6.4	
$KMgF_3$	2.070(20)	314.0(1)	308.3(4)	0.8(1)	6.4(2)	7.2(2)	6.5(5)[b]
		324	324	0	6.6	6.5	
$RbCdF_3$	2.124(12)	314.4(1)	309.5(3)	0.7(1)	4.0(1)	4.7(1)	4.7(2)[c]
		324	324	0	4.5	4.5	

[a] Reference 24.

[b] Reference 35.

[c] Reference 36.

$a = 6.3 \pm 0.1$,[24] 6.5 ± 0.5,[35] and 4.7 ± 0.2,[36] in 10^{-4} cm^{-1}, respectively. By taking a SO constant $\zeta = 324$ $cm^{-1} < \zeta_{3d}$, a is calculated to be 6.4, 6.5, and 4.5, in 10^{-4} cm^{-1}, respectively. The results obtained are in good agreement with the experimental findings.

The obtained values of ζ_{te} and ζ_{tt} as well as the reported electrostatic and CF parameters enables us to evaluate a, a_{SO},and $a_{CF\text{-}SO}$ in the extended CF model. a is obtained to be 6.5 ± 0.1 for Mn^{2+}:$KZnF_3$, 7.2 ± 0.2 for Mn^{2+}:$KMgF_3$, and 4.7 ± 0.1 for Mn^{2+}:$RbCdF_3$, in units of 10^{-4} cm^{-1}, consistent with the experiments as well. The SO-only effect has a contribution $a_{SO} = 0.7 \times 10^{-4}$–$0.8 \times 10^{-4}$ cm^{-1} for the crystals, which is about 15% of the total contribution. The CF-SO combined effect plays the most important role in affecting the ZFS of these crystals.

For the lattices under consideration, the SO constants ζ_{te} and ζ_{tt} are a little different from each other as a consequence of the high ionic bonds and the small value of ζ_L (240 cm^{-1}) of the ligand F^-. In fact, according to Francisco and Pueyo,[17] the values of ζ_{te} remain around 314 cm^{-1}, ζ_{tt} around 309 cm^{-1}, and the difference $\zeta_{te} - \zeta_{tt}$ around 5 cm^{-1}, for Mn^{2+} ions doped in fluoroperovskites whose R values vary from 2.070 to 2.124 Å. Therefore, for most purposes, the SO constants can be reasonably considered to be identical and the CF model is capable of providing satisfactory interpretations for the spectroscopic properties.

VII. SUMMARY

Owing to the mixing of atomic orbitals of the magnetic and ligand ions, there are two independent SO constants ζ_{te} and ζ_{tt} which are dependent on the covalency and SO constant of the p orbital of the ligands, for a $3d^n$ ion in a cubic crystal. The values of the constants ζ_{te} and ζ_{tt} are in general different from each other and less than the free-ion value ζ_{3d} of the open $3d^n$-shell electrons. The combined interaction of CF and SO couplings in the $3d^5$ configuration contributes at fourth and higher orders to the ZFS parameter a of the ground state $^6A_1$ a value $a_{CF\text{-}SO}$, and the SO interaction alone does so in a similar way with a contribution a_{SO}. Independent of CF potential, the SO-only effect a_{SO} is a function of the difference between ζ_{te} and ζ_{tt}; it is great for a large value of the difference and zero when $\zeta_{te} = \zeta_{tt}$. For a given crystal, ZFS depends on the SO constants and the CF parameter. In the case of a slight mass of ligands, highly ionic bonds, and a strong CF potential the CF-SO combined effect is predominant over ZFS. In the opposite case, however, the SO-only effect is most important. In the intermediate case, both effects have to be taken into account. The CF model, which assumes $\zeta = \zeta_{te} = \zeta_{tt}$, is capable of obtaining a value of $a_{CF\text{-}SO}$, but approximately; it can work satisfactorily for the cases where the ligands are slight and the bonds are highly ionic.

The SO constants ζ_{te} and ζ_{tt} contribute to ZFS in different ways because of the different interaction processes. All the interaction processes which contribute to ZFS are in association with a coupling between states of different configurations $t_2^m e^{5-m}$. Further, the processes in which the couplings are all between states of different configurations make a positive contribution proportional to ζ_{te}^4. Other processes contribute negatively through terms in ζ_{tt}^k $(k = 1,2,3)$. The total value is thus determined by the relative magnitude of these two parts. In particular, the value of a can be significantly greater than the CF-model limitation value $a(\zeta_{3d})$ calculated by assuming $\zeta = \zeta_{te} = \zeta_{tt} = \zeta_{3d}$.

The value of $a(\zeta_{3d})$ is always positive in real crystals. Comparison between it and the observed a value can serve as an indication of the role of the SO-only effect: If a has been observed to be greater than $a(\zeta_{3d})$, the SO-only effect must be important and the CF model must fail to account for the observed value. Nevertheless, the SO-only effect exits always in real crystals because of the different contributions of the SO constants. Therefore the extended CF model is more useful in the study of the ZFS of $^6S(3d^5)$ ions.

ACKNOWLEDGMENTS

This work was supported by the Educational Committee of China, by the National Natural Sciences Foundation of China (Grant No. 28970142), and by the Committee of Science and Technology of Sichuan Province.

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