Contributions to zero-field splitting from spin triplets of $3d^4$ and $3d^6$ ions in tetragonal symmetry

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In this paper, the perturbation formulas for the zero-field splitting (ZFS) parameters of $3d^4$ and $3d^6$ ions in tetragonal symmetry are derived taking into account all the excited spin-triplet states ${}^3L$ $(L=P,D,F,G,H)$, in the strong-field scheme. The contribution of the spin triplets to the ZFS and the validity of the ${}^5D$ approximation for $3d^4$ ions at tetragonal sites are investigated. The results show that the spin-triplet contribution to the ZFS is not negligible, and the validity of ${}^5D$ approxmation is highly limited in general, although a great deal of early studies of the ZFS for $3d^4$ and $3d^6$ ions in crystals were based on the ${}^5D$ approximation. Applications are made to Fe^{4+} ions in $CdSiP_2$ and Cr^{2+} ions in Rb_2CrCl_r, and the obtained results are in good agreement with the experimental data. The contribution of spin triplets is found to be either comparable to or larger than that of ${}^5D$ state in these crystals.

I. INTRODUCTION

Zero-field splitting (ZFS) for $3d^4$ and $3d^6$ ions at tetragonal symmetry sites have been studied by many authors (see, e.g., Refs. 1–17). However, most of these works were carried out within spin-quintet ${}^5D$ states,[1–2,6–10,12–15] namely, the ${}^5D$ approximation; i.e., the contributions of the excited spin-triplet and spin-singlet states were neglected. The perturbation formulas in the ${}^5D$ approximation for the ZFS parameters of $3d^4$ and $3d^6$ at tetragonal sites were given[7–10] for all possible ground-orbital-singlet cases. Early in the 1970's, Vallin and Watking investigated the ZFS of the Cr^{2+} ($3d^4$) ion in II-VI lattices.[3–5] They considered the spin-orbit (s.o.) interaction within ${}^5D$ and the spin-spin coupling within the excited triplets as an average energy, and obtained a little of the spin-triplet contribution. More recently, a theoretical study[11] for the Fe^{2+} ion in orthopyroxene indicated that the spin-triplet contribution to ZFS is larger than the spin-quintet one in this crystal. Recently, Rudowicz, Du, and Yeng[16] dealt with the crystal-field (CF) energy levels and fine-structure splittings arising from the s.o. interaction for Fe^{2+} and Fe^{4+} in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$, and showed that the contribution of the spin singlets to the fine-structure splittings of the ground state is negligible; however, the spin-triplet contribution cannot be neglected. And the analysis of ZFS of the ground state of $3d^4$ and $3d^6$ ions within the ${}^5D$ approximation may be generally not valid.

In the present paper, we go beyond the ${}^5D$ approximation and consider the ZFS parameters, taking into account all the spin-triplet states ${}^3L$ (L = P, D, F, G, and H) for $3d^4$ and $3d^6$ ions in tetragonal symmetry by a perturbation approach in a strong-field scheme. The perturbation formulas for the axial ZFS parameter D are given up to fourth-order terms. D is calculated as a function of the CF parameters, for $3d^4$ ions at tetragonal sites, showing that the contribution of the excited spin triplets is large in most of the range of the CF parameters considered. Numerical calculations of the ZFS parameter D for Fe^{4+}: $CdSiP_2$ and Rb_2CrCl_4 show again the important spin-triplet contribution. Thus many previous works based on the ${}^5D$ approximation should be reconsidered.

II. FORMULAS OF ZFS FOR $3d^4$ AND $3d^6$ IONS IN TETRAGONAL SYMMETRY

In the strong CF coupling scheme, the Hamiltonian for $3d^4$ and $3d^6$ ions in tetragonal symmetry can be written as

$$H=H_0+H' , \qquad (2.1)$$

with

$$H_0=H_c(Dq)+H_t^a(\delta,\mu)+H_e^a(B,C) , \qquad (2.2)$$

$$H'=H_t^b(\delta,\mu)+H_e^b(B,C)+H_{\mathrm{s.o.}}(\xi) , \qquad (2.3)$$

where H_c, H_t^a, H_t^b, H_e^a, H_e^b, and $H_{\mathrm{s.o.}}$ are the cubic CF, the diagonal (H_t^a) and the off-diagonal (H_t^b) tetragonal CF, the diagonal (H_e^a) and the off-diagonal (H_e^b) electrostatic Coulomb interaction, and the s.o. interaction terms, respectively. Dq is the cubic CF parameter, δ and μ are the tetragonal distortion CF parameters, B and C the Racah electrostatic parameters, and ξ denotes the s.o. coupling constant. If the s.o. interaction $H_{\mathrm{s.o.}}$ in Eq. (2.3) is not considered, for $3d^4$ and $3d^6$ ions in tetragonal symmetry, there are 4 spin-quintet ($S=2$) terms (${}^5\Gamma$) and 33 spin-triplet ($S=1$) terms (${}^3\Gamma$) ($\Gamma=A_1$, A_2, B_1, B_2, and E, the irreducible representations, for the tetragonal point groups C_{4V}, D_4, and D_{2d}). The ${}^5B_2$ being the lowest has been found[8] in many crystals such as Rb_2FeCl_4, $FeNb_2O_6$, $Fe(HCOO)_2\cdot 2\,H_2O$, Cr:GaAs, $CrSO_4\cdot 5H_2O$, and so on. We therefore deal with this case.

For $3d^4$ and $3d^6$ ions at tetragonal sites, the ZFS Hamiltonian is

$$H_{\mathrm{ZFS}}=DS_z^2\ , \tag{2.4}$$

where D is the axial ZFS parameter. In the present work, the zero-order wave functions transforming as the irreducible representations of the O_h point group are combined with the one-electron wave function t_{2g} and/or e_g. Following perturbation theory,[18,19] a detailed derivation yields formulas of D up to fourth-order terms for the ground state $^5B_2$. All the excited spin-triplet states are considered. The contribution of first-order perturbation processes to D vanishes. The nonzero contributions from second- to fourth-order processes are obtained. We separate them into two parts: D(I) and D(II). D(I) is just the contribution of ^5D, and D(II) is that of the combination of the spin-triplet states ^3L and spin quintet ^5D. The formulas can be written as

$$D=D(\mathrm{I})+D(\mathrm{II})\ , \tag{2.5}$$

$$D(\mathrm{I})=\frac{\xi^2}{4}\left[-\frac{1}{D_2}+\frac{1}{4D_3}\right]-\frac{\xi^3}{16}\left[\frac{1}{D_2D_3}+\frac{1}{2D_3^2}\right]+\frac{\xi^4}{1792}\left[\frac{27}{D_1D_3^2}+\frac{21}{D_2D_3^2}+\frac{496}{D_2^3}-\frac{43}{D_3^3}\right]\ , \tag{2.6}$$

$$\begin{aligned}
D(\mathrm{II})=-\xi^2&\left[-\frac{1}{9D_{15}}-\frac{1}{9D_{16}}-\frac{1}{36D_{17}}-\frac{1}{9D_{18}}-\frac{1}{18D_{19}}+\frac{1}{24D_{26}}+\frac{1}{8D_{27}}\right.\\
&\left.+\frac{1}{8D_{28}}+\frac{1}{24D_{29}}+\frac{1}{24D_{30}}+\frac{1}{48D_{33}}+\frac{1}{4D_{35}}+\frac{1}{12D_{36}}\right]\\
&+\xi^3\left[-\frac{3}{8D_2D_{27}}+\frac{1}{8D_2D_{29}}+\frac{1}{16D_2D_{33}}-\frac{1}{12D_3D_{15}}-\frac{1}{12D_3D_{16}}+\frac{1}{96D_3D_{17}}+\frac{1}{24D_3D_{18}}\right.\\
&+\frac{1}{48D_3D_{19}}+\frac{1}{18D_{15}D_{29}}+\frac{1}{9D_{16}D_{29}}+\frac{1}{18D_{16}D_{33}}-\frac{1}{9D_{16}D_{36}}-\frac{1}{24D_{17}D_{27}}+\frac{1}{72D_{17}D_{29}}\\
&+\frac{1}{48D_{17}D_{33}}-\frac{1}{12D_{18}D_{27}}-\frac{1}{36D_{18}D_{29}}+\frac{1}{12D_{18}D_{32}}+\frac{1}{12D_{19}D_{26}}-\frac{1}{36D_{19}D_{29}}-\frac{1}{72D_{19}D_{33}}\\
&-\frac{1}{18D_{19}D_{36}}-\frac{1}{8D_{26}D_{27}}+\frac{1}{24D_{26}D_{29}}-\frac{1}{24D_{26}D_{32}}-\frac{1}{8D_{27}D_{28}}-\frac{1}{8D_{27}D_{32}}-\frac{1}{8D_{28}D_{29}}\\
&+\frac{1}{8D_{28}D_{32}}+\frac{1}{24D_{29}D_{32}}+\frac{1}{24D_{32}D_{33}}-\frac{1}{4D_{32}D_{35}}-\frac{1}{12D_{32}D_{36}}-\frac{1}{96D_{33}^2}-\frac{1}{8D_{35}^2}\\
&\left.-\frac{1}{4D_{35}D_{36}}+\frac{1}{24D_{36}^2}\right]\\
&+B\xi^2\left[\frac{8}{3D_{15}D_{16}}-\frac{2}{9D_{17}D_{18}}+\frac{2}{3D_{18}D_{19}}-\frac{5}{4D_{26}D_{27}}+\frac{1}{4D_{26}D_{32}}-\frac{1}{2D_{26}D_{35}}-\frac{5}{4D_{27}D_{32}}\right.\\
&\left.+\frac{5}{4D_{28}D_{29}}+\frac{1}{4D_{28}D_{33}}+\frac{1}{2D_{28}D_{36}}+\frac{1}{4D_{29}D_{33}}-\frac{1}{2D_{32}D_{35}}+\frac{1}{2D_{33}D_{36}}\right]\\
&+\frac{(B+C)\xi^2}{2D_{27}D_{35}}+\frac{(3B+C)\xi^2}{6D_{29}D_{36}}-\frac{\mu\xi^2}{9D_{15}D_{18}}+\frac{2\delta\xi^2}{3D_{16}D_{19}}+D(\mathrm{II})^{(4)}\ ,
\end{aligned} \tag{2.7}$$

where $D(\mathrm{II})^{(4)}$ is the fourth-order perturbation terms of D(II). There are about a thousand terms in $D(\mathrm{II})^{(4)}$. The numerical calculations show that the contribution of $D(\mathrm{II})^{(4)}$ to D is negligible, and we have not given the expression for $D(\mathrm{II})^{(4)}$. D_i are the zero-order energies. The designations of the states and energies are given in Table I. (Only 16 spin triplets are listed; the others appearing only in $D(\mathrm{II})^{(4)}$ are not given. The relationships of the representation notations between the cubic and tetragonal fields can be found in Table A.11 of Ref. 27.)

III. SPIN-TRIPLET CONTRIBUTION TO ZFS FOR $3d^4$ IONS

According to a recent work[15] and the diagonalization of the present Hamiltonian matrix including the CF and electrostatic interactions ($H_c+H_t+H_e$), we find that with the variations of the CF parameters Dq, δ, and μ the ground states may be exchanged within $^5A_1$, $^5B_1$, $^5B_2$, ^5E, and $^3\Gamma_i$ states. The $^5B_2$ ground state for the $3d^4$ ion

TABLE I. Definition of the states and energies for $3d^4$ and $3d^6$ ions in tetragonal symmetry.

$D_1 = W(^5A_1) - W(^5B_2) = -10Dq + \mu$
$D_2 = W(^5B_1) - W(^5B_2) = -10Dq$
$D_3 = W(^5E) - W(^5B_2) = \delta$
$D_{15} = W(a\,^3B_1) - W(^5B_2) = -10Dq + \mu/2 + 13B + 4C$
$D_{16} = W(b\,^3B_1) - W(^5B_2) = \frac{1}{35}(22\delta - \mu) + 19B + 7C$
$D_{17} = W(c\,^3B_1) - W(^5B_2) = -10Dq + 8B + 4C$
$D_{18} = W(d\,^3B_1) - W(^5B_2) = -10Dq + \frac{1}{2}\mu + 11B + 4C$
$D_{19} = W(e\,^3B_1) - W(^5B_2) = \frac{4}{3}\delta + 10B + 4C$
$D_{26} = W(a\,^3E) - W(^5B_2) = -10Dq + \frac{3}{4}\mu + 10B + 4C$
$D_{27} = W(b\,^3E) - W(^5B_2) = -10Dq + \frac{1}{4}\mu + 18B + 6C$
$D_{28} = W(c\,^3E) - W(^5B_2) = -10Dq + \frac{1}{4}\mu + 12B + 4C$
$D_{29} = W(d\,^3E) - W(^5B_2) = -10Dq + \frac{3}{4}\mu + 16B + 6C$
$D_{30} = W(e\,^3E) - W(^5B_2) = \delta + 20B + 6C$
$D_{31} = W(f\,^3E) - W(^5B_2) = \delta + 12B + 4C$
$D_{32} = W(g\,^3E) - W(^5B_2) = \delta + 10B + 4C$
$D_{33} = W(h\,^3E) - W(^5B) = \delta + 8B + 4C$
$D_{34} = W(i\,^3E) - W(^5B_2) = \delta + 12B + 4C$
$D_{35} = W(j\,^3E) - W(^5B_2) = 10Dq + \frac{3}{7}\delta - \frac{1}{4}\mu + 5(B + C)$
$D_{36} = W(k\,^3E) - W(^5B_2) = 10Dq + \frac{1}{4}(4\delta - 3\mu) + 13B + 5C$

$^5B_2 = [t_2^2e^2, {}^5T_2\zeta]$,	$^5E = [t_2^2e^2, {}^5T_2(\xi,\eta)]$,
$^5A_1 = [t_2^3e, {}^5E\theta]$,	$^5B_1 = [t_2^3e, {}^5E\varepsilon]$,
$a\,^3B_1 = [t_2^3e, {}^3A_2]$,	$b\,^3B_1 = [t_2^2e^2, {}^3A_2]$,
$c\,^3B_1 = [t_2^3(^4A_2)e, {}^3E\varepsilon]$,	$d\,^3B_1 = [t_2^3(^2E)e, {}^3E\varepsilon]$,
$e\,^3B_1 = [t_2^2e^2, {}^3E\varepsilon]$,	
$a\,^3E = [t_2^3(^2T_1)e, {}^3T_1(x,y)]$,	$b\,^3E = [t_2^3(^2T_2)e, {}^3T_1(x,y)]$,
$c\,^3E = [t_2^3(^2T_1)e, {}^3T_2(\xi,\eta)]$,	$d\,^3E = [t_2^3(^2T_2)e, {}^3T_2(\xi,\eta)]$,
$e\,^3E = [t_2^2(^3T_1)e^2(^1A_1), {}^3T_1(x,y)]$,	$f\,^3E = [t_2^2(^3T_1)e^2(^1E), {}^3T_1(x,y)]$,
$g\,^3E = [t_2^2(^1T_2)e^2(^3A_2), {}^3T_1(x,y)]$,	$h\,^3E = [t_2^2(^3T_1)e^2(^3A_2), {}^3T_2(\xi,\eta)]$,
$i\,^3E = [t_2^2(^3T_1)e^2(^1E), {}^3T_2(\xi,\eta)]$,	$j\,^3E = [t_2e^3, {}^3T_1(x,y)]$,
$k\,^3E = [t_2e^3, {}^3T_2(\xi,\eta)]$	

is maintainable when the values of Dq, δ, and μ are as follows.[17]

$$-Dq:\ 0\text{–}2000\ \text{cm}^{-1}\ \text{for}\ \mu>0\ \text{or}\ -\mu/10\text{–}2000\ \text{cm}^{-1}\ \text{for}\ \mu<0;\quad \delta:\ 0\text{–}15\,000\ \text{cm}^{-1};\quad \mu:\ -10|Dq|\text{–}10\,000\ \text{cm}^{-1}. \tag{3.1}$$

In our recent work,[17] the convergence of the ZFS perturbation formulas in the ^5D approximation for $3d^4$ ions at tetragonal sites has been studied. The ranges of the values of Dq, δ, and μ, in which the perturbation formulas in the ^5D approximation are valid, are as follows:

$$-Dq:\ \xi\text{–}2000\ \text{cm}^{-1}\ \text{or}\ -\mu/10\text{–}2000\ \text{cm}^{-1}\ (\text{when}\ -\mu/10>\xi);\quad \delta:\ \tfrac{5}{2}\xi\text{–}15\,000\ \text{cm}^{-1};\quad \mu:\ -10|Dq|\text{–}10\,000\ \text{cm}^{-1}. \tag{3.2}$$

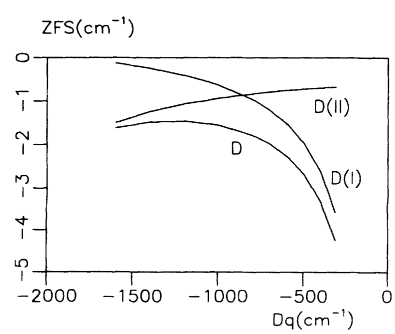

FIG. 1. Dependence of ZFS parameters on Dq. Values of $\delta = 12\,507$ and $\mu = -3036\ \text{cm}^{-1}$ are used.

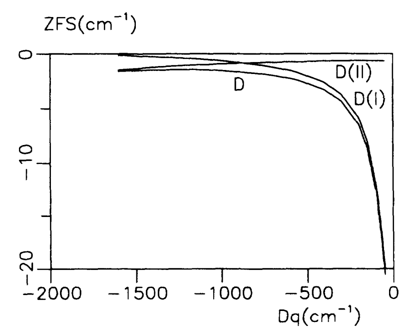

FIG. 2. Dependence of ZFS parameters of Dq. Values of $\delta = 4500$ and $\mu = 2500\ \text{cm}^{-1}$ are used.

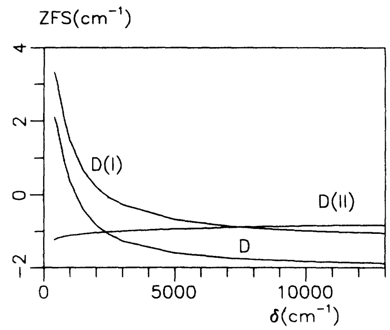

FIG. 3. Dependence of ZFS parameters on δ. Values of $-Dq=1017$ and $\mu=-3036$ cm^{-1} are used.

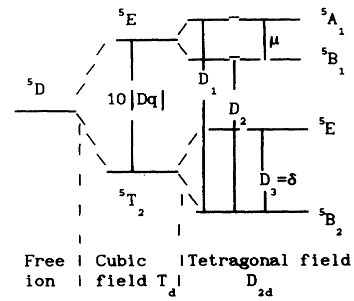

FIG. 5. Energy levels ($^5\Gamma_i$) of $3d^4$ ions in a tetragonal crystal field.

Using Eqs. (2.5)–(2.7) and (3.2) we calculate D, D(I), and D(II) versus Dq, δ, and μ. The results are shown in Figs. 1–4. In the calculations, the values of $B=810$, $C=3565$, and $\xi=200$ (cm^{-1}) (Ref. 20) are used.

The variations of D(I), D(II), and D with Dq are shown in Figs. 1 and 2 for $\delta=12\,507$ and $\mu=-3036$ cm^{-1} (Ref. 20) and $\delta=4500$ and $\mu=2500$ cm^{-1},[21] respectively. From these figures we find that when the value of $|Dq|$ increases the value of D(I) decreases, whereas D(II) increases. This means that the larger the value of $|Dq|$, the larger are the spin-triplet contributions to the ZFS parameter D. This result is the same as that obtained by a recent similar study[22] which deals with the spin-triplet contribution to ZFS by diagonalization of the Hamiltonian matrices. In most of the range of Dq ($-Dq\approx 500$–1500 cm^{-1}) considered, the values of D(II) are large. When $|Dq|>1000$ cm^{-1}, D(II) is larger than D(I). In the area of $-Dq>1500$ cm^{-1}, D(I) tends to zero and D(II) becomes the major contribution to D. The cubic CF parameter $|10Dq|$) is the splitting between $^5T_{2g}$ and ^5E_g (see Fig. 5). From Table I we can see that with the increasing of $|Dq|$ the energies of the quintet states $^5A_1$ and $^5B_1$ will increase, whereas those of triplet states $j\,^3E$ and $k\,^3E$ decrease. This means that with the increasing of $|Dq|$ the contribution of excited triplet states ^3L to D will increase and that of ^5D will decrease. When the energies of some triplet states $^3\Gamma_i$ are lower than that of $^5\Gamma_i$, $|D(\mathrm{II})|$ may become larger than $|D(\mathrm{I})|$. From these figures we can find that only in the area of small Dq ($-Dq<400$ cm^{-1}) is the ^5D approximation valid. In the range of $-Dq\cong 500$–1500 cm^{-1}, the ^5D approximation is no longer valid and the spin-triplet contribution should be considered.

The dependence of D(I), D(II), and D on δ is shown in Fig. 3. Here the values of $-Dq=1017$, $\mu=-3036$ cm^{-1} (Ref. 20) are used. From Fig. 3 we can find that when the value of δ increases the value of D(I) decreases; however, the variation of D(II) is very small. Only for small δ ($\delta<700$ cm^{-1}) does the $|D(\mathrm{I})|$ far exceed $|D(\mathrm{II})|$. In most of the range ($\delta\cong 700$–$13\,000$ cm^{-1}), the D(II) is large enough to compare with D(I). From the definition of D_3 in Table I, one can see that δ is the tetragonal splitting of $^5T_{2g}$ into $^5B_2$ and ^5E (see Fig. 5). When Dq and μ are fixed, the ^5E level will go up with δ increasing, and then D(I) will decrease. However, the influence of δ on the energies of most of the spin triplets in Table I is small, and the variation of D(II) is small with δ increasing. When the energy of ^5E becomes large enough, the influence of ^5E on the ground-state splitting becomes negligible and D(I) tends to a constant (see Fig. 3). From this figure we find that in most of the range considered ($\delta\approx 700$–$12\,000$ cm^{-1}) the contribution of excited triplet states to ZFS is not negligible.

Figure 4 shows the variation of D(I), D(II), and D with the change of μ. The values of $-Dq=1017$, $\delta=12\,507$ cm^{-1} (Ref. 20) are used. From Fig. 4 we find that the variations of D(I), D(II), and D are very small with the change of μ. However, in all the change range of μ the value of D(II) is comparable to D(I). From the definitions of D_1 and D_2 in Table I, one can see that μ is the tetragonal splitting of ^5E_g into $^5B_1$ and $^5A_1$ (see Fig. 5). From Eq. (2.6) it can be seen that the major contribution to D(I) is from $^5B_1(D_2)$ and $^5E(D_3)$, and the influence of $^5A_1$, i.e., μ, on D(I) is very small. However, from Table I and Eq. (2.7), it can be seen that the parameter μ appears mostly in D(II) and then the influence of μ on the contribution of spin triplets is larger than that of spin quintets (see Fig. 4). Figure 4 shows that in most of the range of μ considered, the contribution of spin-triplet states to the ZFS D is not negligible.

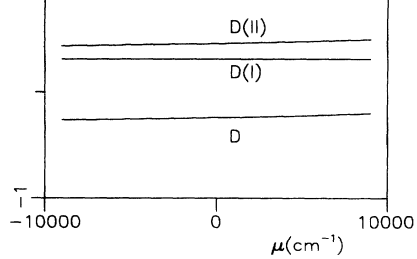

FIG. 4. Dependence of ZFS parameters on μ. Values of $-Dq=1017$ and $\delta=12\,507$ cm^{-1} are used.

TABLE II. Crystal-field and Racah parameters, and spin-orbit and spin-spin coupling constants (in cm^{-1}).

	Dq	δ	μ	B	C	ξ	ρ
Rb_2CrCl_4 [a]	−1017	12507	−3036	810	3565	240	0.30
Fe^{4+}:$CdSiP_2$	−850 [b]	1200 [c]	760 [b]	1098 [c]	4280 [c]	494 [b]	0.25 [b]

[a]Reference 20.
[b]Reference 22.
[c]This work.

Up until now, the conclusion is that (i) the contribution of excited triplet states to ZFS is not negligible and (ii) the validity of the ^5D approximation is very limited.

IV. CALCULATION OF ZFS FOR Fe^{4+} AND Cr^{2+} IONS

A. Fe^{4+}: $CdSiP_2$

The two different $S=2$ electron paramagnetic resonance (EPR) centers observed in Fe-doped $CdSiP_2$ are assigned to Fe^{2+} ($3d^6$) and Fe^{4+} ($3d^4$) substituting for Cd^{2+} and Si^{4+}, respectively. Kaufmann[23] investigated the EPR and optical-absorption spectra of Fe^{4+} at tetragonal sites in $CdSiP_2$ and obtained the ZFS parameter $D=1.822$ cm^{-1} and the energy levels $D_1=9260$ cm^{-1} and $D_2\approx 8500$ cm^{-1}. From these data the values of $-Dq=850$ and $\mu=760$ cm^{-1} can be obtained. Using the ^5D approximation formula

$$D=D(I)-3\rho \tag{4.1}$$

and Eq. (2.6) together with $D=1.822$ cm^{-1} and $D_2=8500$ cm^{-1}, he obtained $D_3(=\delta)\approx 1100$ cm^{-1}. Since the value of δ was obtained in the ^5D approximation, it may be unsuitable. We take $\delta=1200$ cm^{-1} to fit the experiment data. From the average covalency approximation model,[24–26] the Racah parameters B and C and the spin-orbit coupling constant ξ can be obtained by

$$B=k^2B_0\ ,\quad C=k^2C_0\ ,\quad \xi=k\xi_0\ , \tag{4.2}$$

where k is the average covalency reduction factor and $B_0=1144$, $C_0=4459$, and $\xi_0=514$ (cm^{-1}) (Ref. 27) are for free ions Fe^{4+}. In Ref. 23 the value of $\xi=494$ cm^{-1} for Fe^{4+}: $CdSiP_2$ was used by fitting the optical spectrum. And then the values of $k=\xi/\xi_0=0.96$, $B=1098$ cm^{-1}, and $C=4280$ cm^{-1} are obtained from Eq. (4.2). Using these values (shown in Table II), we obtain the ZFS parameters D(I), D(II), and D listed in Table III. The result of D is in good agreement with the experiment. From Table III one can find that D(II) is larger than D(I) and the value of $|D(\mathrm{II})/D(\mathrm{I})|$ is about 1.75, i.e., the spin-triplet contribution to D is larger than the spin-quintet contribution. This shows that the ^5D approximation is not valid in the crystal.

B. Rb_2CrCl_4(Cr^{2+})

The site symmetry of Cr^{2+} in Rb_2CrCl_4 is tetragonal. Rudowicz *et al.*[20] obtained the values of the CF parameters (B_2^0,B_4^0,B_4^4), Racah parameters (B,C), spin-orbit coupling constant (ξ), and spin-spin coupling constant (ρ) by fitting the optical spectra, as listed in Table II in which the parameters (B_2^0,B_4^0,B_4^4) have been transformed to (Dq, δ, μ). Using these values, we calculate D from Eqs. (2.5)–(2.7). The results are listed in Table III. Our numerical result $D=-2.22$ cm^{-1} is in good agreement with that of diagonalization calculation[20] and experiment.[28] From Table III one can find that D(II) is comparable to D(I); the contribution of spin triplets [can see also the value of $D(\mathrm{II})/D(\mathrm{I})=0.17$] is important.

V. CONCLUSION

In this paper, taking account of all spin-triplet states, we derive the perturbation formulas of the ZFS parameter D up to fourth-order terms for the $^5B_2$ ground state of $3d^4$ and $3d^6$ ions in tetragonal symmetry. A series of calculations of D versus the CF parameters Dq, δ, and μ for $3d^4$ ions at tetragonal sites shows that the contributions of spin triplets to the ZFS parameter D are generally not negligible. The ^5D approximation is valid only in a very small part of the range with small $|Dq|$ and small δ; how-

TABLE III. Zero-field splitting parameter D [in cm^{-1}, except D(II)/D(I), dimensionless].

	D(I)	D(II)	$D_{(\mathrm{II})}/D_{(\mathrm{I})}$	$D\rho$	D	Experiments	
Rb_2CrCl_4	−1.14	−0.19	0.17	−0.90	−2.22	−2.040 [a]	−2.054 [b]
Fe^{4+}:$CdSiP_2$	1.50	−2.63	−1.75	−0.75	−1.88	±1.822 [c]	

[a]Reference 28.
[b]Reference 20.
[c]Reference 22.

ever, in these ranges, the convergence of these perturbation formulas should be considered. And then the validity of the ^5D approximation is very limited. The numerical results of the ZFS in Rb_2CrCl_4 and Fe^{4+}:$CdSiP_2$ show again the very important spin-triplet contribution.

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