Rank-four spin-Hamiltonian parameters of a $3d^5$ ion

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Crystal-field theory is applied to the study of the rank-four spin-Hamiltonian parameters a and F of a ^6S-state ion in tetragonal symmetry. Fifth-order perturbation expressions are derived for the parameters and are further simplified, using the perturbation procedure suggested by Macfarlane and Zdansky. It is shown that the tetragonal field components contribute to the "cubic" splitting parameter a value, a', which is roughly equal to $-(1/2)F$, suggesting that one cannot omit the low-symmetric-field effect in the calculation of a unless he has confirmed the axial term F to be negligibly small compared with it. Both a' and F arise mainly from the interaction of the ground state ^6S with the excited states $^4T_1$, $^4T_2$, ^4E, $^2T_2$, and ^2E via spin-orbit coupling. The two tetragonal field components, B_{20} and B'_{40}, have a similar significance in affecting a', and F, unlike the case of the rank-two term D, where B_{20} plays a negligible role. The crystal-field model suggests F to be identical in sign to D. Numerical calculations are performed for Mn^{2+} ions in K_2ZnF_4 and K_2MgF_4 of D_{4h} symmetry and for Fe^{3+} ions at the tetrahedral D_{2d} sites in YGaG, YA1G, LuGaG, and Lu-A1G, (where G represents garnet), and the results are reasonable.

I. INTRODUCTION

The rank-four spin-Hamiltonian parameters a and F, as well as the rank-two term D, are important in describing the ESR spectra and the single-ion magnetocrystalline anisotropy. For $3d^5$ ions, the interpretation of the parameters is considerably complicated due to the lack of the orbital angular momentum in the ground state ^6S. During the past decades much work has been devoted to the study of the rank-two terms (see the review in Ref. 1), but only a few dealt with the calculation of the rank-four parameters,[2-9] especially in the case of low symmetry.[6] This is probably because they are very difficult to calculate.

Cubic symmetry serves as the simplest case, where all vanish except for a, the cubic splitting parameter. In order to calculate it, one may diagonalize the energy matrices, getting an accurate result,[3-5,8,9] or approach it with an available perturbation procedure.[7,9] A recent work has shown the success of the current crystal-field theory.[9]

Up until now it has not been known how the low-symmetric-field components affect the "cubic" term a and give rise to an axial splitting F, when the symmetry is lower than cubic. Dealing with this problem is the main aim of this work. We confine ourselves to tetragonal symmetry.

No accurate result can be expected for any spin-Hamiltonian parameter of a d^5 ion in symmetries lower than cubic. Actually, because of the Kramers degeneracy, we have two energy differences in the ground state ^6S but three or more independent parameters. Only approximate results are expected for a and F, and the perturbation theory is useful.

A perturbation calculation has been performed by Sato et al.[6] However, their results are unsatisfactory and even incorrect. First, among all of the 40 excited states only two, $^4T_1(t_2^4(^3T_1)e)$ and $^2T_2(t_2^5)$, were involved in their calculation. The two states may play an important role, but there is no physical reason allowing one to omit others. In fact, as we will show in Sec. II, many of the states they have omitted are not negligible. Second, their results do not fit the self-complementary property, which requires that an expression for half-filled ions remains unchanged upon simultaneously changing the signs of the spin-orbit coupling constant and the crystal-field parameters.

In the present work we employ the perturbation procedure developed by Macfarlane[10] and Zdansky[11] for F-state ions. this procedure has been confirmed for S-state ions.[9,12] All excited states will be taken into calculation and analytical expressions will be derived and simplified for a and F. Interesting consequences include (i) that the low-symmetric-field components contribute to a, a value denoted with a', which is not negligible in general, (ii) that a' roughly equals $-\frac{1}{2}F$, (iii) that the components B_{20} and B'_{40} contribute to a' and F with a similar significance, and (iv) that the excited states $^4T_1$, ^4E, $^4T_2$, $^2T_2$, and ^2E are important, whereas the others negligible.

A fifth-order perturbation calculation is performed in Sec. II. The obtained formulas are simplified in Sec. IV after a discussion in Sec. III. Section V presents some applications, and a summary is drawn in Sec. VI.

II. CALCULATION

A. Perturbation method

The parameters D, a, and F are defined by the spin-Hamiltonian

$$H_s = D(S_z^2 - \tfrac{35}{12}) + (a/6)(S_\xi^4 + S_\eta^4 + S_\zeta^4 - \tfrac{707}{16})$$

$$+ (7F/36)(S_z^4 - \tfrac{95}{14}S_z^2 + \tfrac{81}{16}) \tag{1}$$

for an ion in the ^6S state. ζ, η, and ξ denote the cubic crystalline axes, and z denotes the symmetric principal one. For crystals of tetragonal symmetry, $\zeta\|z$, $\eta\|y$, and $\xi\|x$. It follows from (1) that

$$a=(2/\sqrt{5})\langle \tfrac{5}{2}|H_s|-\tfrac{3}{2}\rangle , \tag{2}$$

$$F=\tfrac{3}{14}[\langle \tfrac{5}{2}|H_s|\tfrac{5}{2}\rangle +2\langle \tfrac{1}{2}|H_s|\tfrac{1}{2}\rangle -3\langle \tfrac{3}{2}|H_s|\tfrac{3}{2}\rangle]$$

$$-\frac{3}{\sqrt{5}}\langle \tfrac{5}{2}|H_s|-\tfrac{3}{2}\rangle . \tag{3}$$

The Hamiltonian of a ^6S-state ion in a tetragonal field may be written as

$$H=H_0+V_c+V_t+H_{so} . \tag{4}$$

H_0 represents the free-ion Hamiltonian, V_c and V_t are the cubic and the tetragonal parts of a field, respectively, and H_{so} is the spin-orbit interaction. We express[12]

$$V_t=B_{20}C_0^{(2)}+B_{40}'C_0^{(4)} , \tag{5}$$

$$V_c=B_{44}(\sqrt{14/5}C_0^{(4)}+C_4^{(4)}+C_{-4}^{(4)}) , \tag{6}$$

with

$$B_{40}'=B_{40}-\sqrt{14/5}B_{44} . \tag{7}$$

In the strong-field scheme of Sugano et al.,[13] V_c is diagonal, whereas the others are not. We may take the sum of V_c and the diagonal part of H_0 as an unperturbed Hamiltonian and the remaining, including V_t, H_{so}, and the off-diagonal part of H_0, as perturbation terms. This perturbation procedure was first suggested by Macfarlane[10] and Zdansky[11] for F-state ions and has achieved success in the calculation of a in cubic symmetry[9] and D in rhombic symmetry[12] for S-state ions. We expect it to also work well in this case.

B. Perturbation processes

The "cubic" splitting parameter a does not come only from the cubic-field component of a field of low symmetry. The low-symmetric-field components will affect all excited states and so they must have contributions to a. The case is similar to the rank-two axial term D, which comes not only from the axial components but from all other parts of a field.[14] In fact, any component of a field has a contribution to any spin-Hamiltonian parameter.

We may denote the contribution resulting from the cubic component with a_c and that from the low-symmetric part with a':

$$a=a_c+a' . \tag{8}$$

a' vanishes in cubic symmetries.

A calculation of a_c can be made by taking $V_t=0$. This actually corresponds to a purely cubic field and has already been done.[2-9] An available and simple expression of it has been semiempirically given by Yu as[9]

$$a_c=\frac{\zeta^4}{10D_1^2D_2}\left[\frac{3\Delta-C}{B+C}\pm\frac{\zeta B}{10D_2}\right] \tag{9}$$

with

$$D_1=10B+6C-\Delta , $$

$$D_2=15B+10C-2\Delta . $$

B and C are Racah parameters, ζ is the spin-orbit coupling constant, and $\Delta=10|Dq|$ is the cubic-field parameter. The symbol "$\pm$" applies to octahedral and tetrahedral coordinations, respectively. We now leave calculations of a' and F.

Both a and F are fourth-order effects of spin-orbit interaction and so come from fourth- and higher-order perturbations. In the perturbation procedure we are using, the fourth-order involves no V_t and so produces nothing to a'. The next order includes some processes without relation to V_t, also contributing nothing to a' and F. Other processes in consideration are made up of two sets:

I: $^6SH_{so}{}^4T_1H_{so}{}^{2S+1}\Gamma V_t{}^{2S+1}\Gamma H_{so}{}^4T_1H_{so}{}^6S$,

II: $^6SH_{so}{}^4T_1V_t{}^4T_1H_{so}{}^{2S+1}\Gamma H_{so}{}^4T_1H_{so}{}^6S$ (double) ,

where $^{2S+1}\Gamma$ covers all excited states. The next order is expected to contribute a value of 1 order of magnitude less and will be omitted in our calculation.

C. Results

The calculation is very tedious, and only the final results will be presented. However, we would like to point out that the self-complementary property of half-filled configurations is highly helpful and can reduce the calculation greatly.

The d^5 configuration is half filled and so can be regarded either as five d electrons or as five d holes. The two equivalent considerations will induce opposite signs for single-ion operators V and H_{so}, keeping the matrix elements of H_0 unchanged. Therefore, a quantity G that describes properties of d^5 ions must be an even function of ζ and B_{kq}:

$$G(B,C,B_{kq},\zeta)=G(B,C,-B_{kq},-\zeta) , \tag{10}$$

where ζ is the spin-orbit coupling constant and B_{kq} are the crystal-field parameters.

In our fifth-order treatment, a' and F have been linear in $B_{20}\zeta^4$ and $B_{40}'\zeta^4$ and so must be odd functions of Dq. Further, one member can be regarded as a hole for each of the complementary couples, $t_2^4(S\Gamma)e$ and $t_2^2(S\Gamma)e^3$, t_2^5 and t_2e^4, and $t_2^3(S_1,\Gamma_1)e^2(S_2,\Gamma_2)$ and itself, and thus has diagonal elements of both V and H_{so} opposite in sign to those for the other. As a consequence, the diagonal elements of V and H_{so} vanish identically for the configuration $t_2^3e^2$. This feature, together with that indicated by (10), allows us to consider only the processes in connection with the diagonal elements of V_t in the configurations t_2^4e and t_2^5. We denote this contribution with a_+' and F_+ and those from processes in association with the diagonal elements of V_t in $t_2^2e^3$ and t_2e^4 with a_-' and F_-:

$$a'=a_+'+a_-' , \quad F=F_+ +F_- . \tag{11}$$

Obviously, a_+' is complementary to a_-', and also F_+ to F_-; inverting simultaneously the signs of B_{kq} and ζ results in the other:

$a'_-(B,C,Dq,B_{20},B'_{40},\zeta)$

$$=a'_+(B,C,-Dq,-B_{20},-B'_{40},-\zeta),$$
(12)

$F_-(B,C,Dq,B_{20},B'_{40},\zeta)$

$$=F_+(B,C,-Dq,-B_{20},-B'_{40},-\zeta).$$

In the following we give the fifth-order perturbation formulas of a'_+ and F_+. For convenience of discussion we have introduced the notations $a'^{I}_+(S\Gamma)$, $a'^{II}_+(S\Gamma)$, etc., to denote individual contributions from processes related to the excited state $^{2S+1}\Gamma$ in set I or II:

$$F^{I}_+(^4T_2)=\frac{12\zeta^4}{35E^2_6}\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2(-W_2/4+6W_1),$$
(13a)

$$F^{I}_+(^2T_2)=-\frac{\zeta^4}{35}\left\{\frac{72}{E^2_1E^2_8}(W_2-3W_1)+3\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2\left[\frac{1}{E^2_9}\left[6W_1-\frac{W_2}{4}\right]-\frac{7}{4E^2_{10}}W_2\right]\right\},$$
(13b)

$$F^{I}_+(^2E)=-\frac{18\zeta^4}{35E^2_{14}}\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2\left[\frac{W_2}{3}-4W_1\right],$$
(13c)

$$F^{II}_+(^4E)=-\frac{2\zeta^4}{5E^2_1}\left[\left[\frac{1}{E_1}+\frac{1}{E_3}\right]\left[\frac{4}{E_4}+\frac{3}{E_5}\right]-\frac{4}{E_2E_4}\right]W_2,$$
(14a)

$$F^{II}_+(^4T_2)=\frac{\zeta^4}{5E^2_1}\left[\left[\frac{1}{E_1}+\frac{1}{E_2}\right]\left[\frac{3}{E_6}+\frac{2}{E_7}\right]+\frac{2}{E_3E_7}\right]W_2,$$
(14b)

$$F^{II}_+(^2T_2)=-\frac{\zeta^4}{20E^2_1}\left[\frac{1}{E_1}\left[\frac{72}{E_8}+\frac{3}{E_9}+\frac{3}{E_{10}}\right]+\frac{1}{E_2}\left[\frac{3}{E_9}+\frac{3}{E_{10}}-\frac{4}{E_{11}}\right]+\left[\frac{1}{E_1}+\frac{1}{E_3}\right]\left[\frac{2}{E_{11}}+\frac{24}{E_{12}}+\frac{18}{E_{13}}\right]\right]W_2,$$
(14c)

$$F^{II}_+(^2E)=\frac{\zeta^4}{10E^2_1}\left[\frac{1}{E_1}\left[\frac{12}{E_{14}}+\frac{3}{E_{15}}\right]+\frac{1}{E_2}\left[\frac{12}{E_{14}}+\frac{3}{E_{16}}+\frac{4}{E_{17}}\right]+\left[\frac{1}{E_1}+\frac{1}{E_3}\right]\left[\frac{4}{E_{17}}+\frac{6}{E_{18}}\right]\right]W_2,$$
(14d)

$$a'^{I}_+(^4T_2)=-\frac{4\zeta^4}{5E^2_6}\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2W_1,$$
(15a)

$$a'^{I}_+(^2T_2)=\frac{6\zeta^4}{5E^2_1E^2_8}(W_2-2W_1)+\frac{\zeta^4}{20}\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2\left[\frac{4W_1}{E^2_9}-\frac{W_2}{E^2_{10}}\right],$$
(15b)

$$a'^{I}_+(^2E)=\frac{\zeta^4}{10}\left[\frac{1}{E_1}+\frac{1}{E_2}\right]^2\left[\frac{8}{E^2_{14}}\left[\frac{W_2}{3}-W_1\right]-\frac{1}{6E^2_{15}}W_2\right],$$
(15c)

$$a'^{II}_+(S\Gamma)=-\tfrac{1}{2}F^{II}_+(S\Gamma),\quad S\Gamma={}^4E,\ {}^4T_2,\ {}^2T_2,\ {}^2E,$$
(16)

where

$$W_1=\frac{B_{20}}{7},\quad W_2=5\frac{B'_{40}}{21}$$

and E_i are listed in Table I. Others are zero to lowest order.

III. DISCUSSION

Tables II and III show the individual contributions from various processes as functions of Dq. The following interesting points are noted.

(i) Only the excited states $^4T_1$, ^4E, $^4T_2$, $^2T_2$, and ^2E have nonzero contributions to a' and F in the lowest-order treatment. Other states, including $^4A_1$, $^4A_2$, $^2A_1$, $^2A_2$, and $^2T_1$, will affect the parameters in higher orders and must be somewhat important. This is unlike the case

of cubic symmetry, where the spin quartets ^4E and $^4T_2$ are also negligible.[3,9]

The $^4T_1$ state plays a crucial role in the ^6S-state splitting, for it is the only state that couples with the ground state, via the spin-orbit interaction. Any state that cou-

TABLE I. Expressions of E_i. Inversing the sign of Dq gives D_i.

$E_1=10B+6C-10Dq$	$E_{10}=17B+9C-10Dq$
$E_2=19B+7C$	$E_{11}=19B+8C$
$E_3=10B+6C+10Dq$	$E_{12}=23B+8C$
$E_4=13B+5C$	$E_{13}=37B+12C$
$E_5=14B+5C$	$E_{14}=31B+12C-10Dq$
$E_6=18B+6C-10Dq$	$E_{15}=22B+9C-10Dq$
$E_7=13B+5C$	$E_{16}=31B+10C$
$E_8=15B+10C-20Dq$	$E_{17}=19B+8C$
$E_9=27B+9C-10Dq$	$E_{18}=23B+8C$

TABLE II. Contributions to F from various processes, calculated from the fifth-order perturbation formula with $B = 800$ cm^{-1}, $C = 3000$ cm^{-1}, and $\zeta = 300$ cm^{-1}. Lines in F_+(SE) and F(SE) list values evaluated with the simplified expression. All are in units of 10^{-8}.

Dq (cm^{-1})	600	800	1000	1200
$F^I_+ (^4T_2)$	$-0.6W_2+14.4W_1$	$-0.8W_2+19.4W_1$	$-1.1W_2+27W_1$	$-1.6W_2+39W_1$
$F^I_+ (^2T_2)$	$-4.0W_2+12.5W_1$	$-6.6W_2+21W_1$	$-12W_2+38W_1$	$-24W_2+76W_1$
$F^I_+ (^2E)$	$-0.3W_2+3.3W_1$	$-0.3W_2+4.1W_1$	$-0.4W_2+5.2W_1$	$-0.6W_2+6.9W_1$
F^I_+(tot)	$-5W_2+30W_1$	$-8W_2+45W_1$	$-14W_2+70W_1$	$-26W_2+122W_1$
$F^{II}_+ (^4E)$	$-15W_2$	$-19W_2$	$-26W_2$	$-37W_2$
$F^{II}_+ (^4T_2)$	$+7W_2$	$+10W_2$	$+14W_2$	$+20W_2$
$F^{II}_+ (^2T_2)$	$-20W_2$	$-30W_2$	$-47W_2$	$-79W_2$
$F^{II}_+ (^2E)$	$+9W_2$	$+12W_2$	$+17W_2$	$+24W_2$
F^{II}_+(tot)	$-19W_2$	$-27W_2$	$-42W_2$	$-72W_2$
F_+(tot)	$-24W_2+30W_1$	$-35W_2+45W_1$	$-56W_2+70W_1$	$-98W_2+122W_1$
F_+(SE)	$-24W_2+32W_1$	$-36W_2+46W_1$	$-59W_2+73W_1$	$-104W_2+125W_1$
F(SE)	$-20W_2+25W_1$	$-33W_2+40W_1$	$-56W'_2+68W_1$	$-102W_2+121W_1$

ples with $^4T_1$ has, therefore, an effect on a splitting parameter, and one would expect the spin quartets, with energies generally lower than those of the spin doublets, to have a stronger contribution to a and F. They are negligible in the cubic case because they give contributions that almost cancel each other. To a' and F, ^4E and $^4T_2$ contribute in the opposite sign, in set II. Among the spin doublets, $^2T_2(t_2^5)$ has an energy, E_8, that is lowest and couples most strongly with $^4T_1(t_2^4(^3T_1)e)$, having an energy E_1 that is the lowest of the spin quartets and couples most strongly with the ground state ^6S.[15] It contributes the greatest value to a', F, or a_c, as can be seen in (14c), (13b), (15b), and (16) and in Ref. 9.

(ii) Either a' or F increases in magnitude sensitively with increasing $|Dq|$, as a_c (Ref. 9) and D (Ref. 12) do. This is because a stronger field causes the excited states to have lower energy levels and causes them to mix more into the ground state. A second power law of Dq is seen in the rank-two axial term D, whereas a_c varies with Dq in the way $a_c \propto |Dq|^k$ with k being greater than 2 and increasing sensitively with $|Dq|$. A more sensitive Dq

dependence can be seen for a' or F from the comparison between Tables II or III and Table I of Ref. 9, noting that W_2 (or B'_{40}) is proportional to Dq [see Eqs. (17) and (18)]. When we use the power law $G \propto |Dq|^{k_G}$ to describe the Dq dependence of a spin-Hamiltonian parameter G of $3d^5$ ions, we have

$$k_F \approx k_{a'} > k_{a_c} > k_D \ .$$

(iii) F depends on both B_{20} ($=7W_1$) and B'_{40} ($=21W_2/5$); so does a', unlike D, which depends on B'_{40} only,[12] in the lowest-order treatments. The dependence of D on the tetragonal field parameters is controlled by the diagonal element of V_t in the state $^4T_1$, which happens to be independent of B_{20}. However, F and a' relate with all diagonal elements of V_t in the states $^4T_1$, ^4E, $^4T_2$, $^2T_2$, and ^2E, some of which are functions of both B_{20} and B'_{40}.

From the superposition model of crystal fields[16] it follows that

TABLE III. The same as Table II but for a'.

Dq (cm^{-1})	600	800	1000	1200
$a'^I_+ (^4T_2)$	$-6W_1$	$-8W_1$	$-10W_1$	$-15W_1$
$a'^I_+ (^2T_2)$	$2.5W_2-5W_1$	$4W_2-8W_1$	$8W_2-15W_1$	$15W_2-29W_1$
$a'^I_+ (^2E)$	$0.4W_2-1.3W_1$	$0.5W_2-1.6W_1$	$0.5W_2-1.9W_1$	$0.6W_2-2.3W_1$
a'^I_+(tot)	$2.9W_2-12.3W_1$	$4.5W_2-17.6W_1$	$8.5W_2-26.9W_1$	$15.6W_2-46.3W_1$
$a'^{II}_+ (^4E)$	$+7.5W_2$	$+9.5W_2$	$13W_2$	$18.5W_2$
$a'^{II}_+ (^4T_2)$	$-3.5W_2$	$-5W_2$	$-7W_2$	$-10W_2$
$a'^{II}_+ (^2T_2)$	$+10W_2$	$+15W_2$	$+23.5W_2$	$+39.5W_2$
$a'^{II}_+ (^2E)$	$-4.5W_2$	$-6W_2$	$-8.5W_2$	$-12W_2$
a'^{II}_+(tot)	$+9.5W_2$	$+13.5W_2$	$+21W_2$	$+36W_2$
a'_+(tot)	$12.4W_2-12.3W_1$	$18W_2-17.6W_1$	$29.5W_2-26.9W_1$	$51.6W_2-46.3W_1$
a'_+(SE)	$12.4W_2-12.4W_1$	$18.6W_2-17.9W_1$	$30.6W_2-28.4W_1$	$52.4W_2-48.6W_1$
a'(SE)	$10.3W_2-9.7W_1$	$17.1W_2-15.6W_1$	$29.1W_2-26.4W_1$	$53.2W_2-47W_1$

$$W_1 = \frac{4}{7}\overline{A}_2(R_0)\left[\left[\frac{R_0}{R_1}\right]^{t_2} - \left[\frac{R_0}{R_2}\right]^{t_2}\right],$$

$$W_2 = \frac{20}{7}Dq\left[\left[\frac{R_0}{R_1}\right]^{t_4} - \left[\frac{R_0}{R_2}\right]^{t_4}\right] \quad (Dq>0),$$

(17)

for octahedrally coordinated D_{4h}, where R_1 and R_2 are bond lengths in the z axis and in the xy plane and R_0 is a reference one, and that

$$W_1 = \frac{4}{7}\overline{A}_2(3\cos^2\theta - 1),$$

$$W_2 = -\frac{45}{14}Dq(7\cos^2\theta - 5)(3\cos^2\theta - 1) \quad (Dq<0),$$

(18)

for tetrahedrally coordinated D_{2d}, where θ denotes the bond angle. The intrinsic parameter $\overline{A}_2$ is much greater than Dq, so that W_1 and W_2 have values in the same order. This, together with the fact that they carry numerical coefficients comparable to each other, leads us to the conclusion that both W_1 and W_2 are important in affecting a' and F.

(iv) F and a' have values opposite in sign and identical in order of magnitude. Further, Tables II and III indicates a rough relationship between them:

$$a' \approx -\tfrac{1}{2}F .$$

(19)

Equation (16) shows $a' = -\frac{1}{2}F$ for the processes in set II. It is perturbed by the processes in set I, causes (19) to hold roughly. More detailed consideration shows that (19) holds quite well for D_{2d} symmetry, while for D_{4h} one has $|a'/F| > \frac{1}{2}$, as will be presented in Sec. IV. Equation (19) allows us to regard F as a measurement of the low-symmetric-field effect on the "cubic" splitting term a. If F is considerably small compared with a, one may use the cubic-field approximation $(a \approx a_c')$ to calculate a. In the opposite case, one must take into account the low-symmetric-field effect.

(v) F and D are identical in sign, provided that the crystal-field effect governs their signs. According to Yu and Zhao[12] and in a similar treatment we have

$$D(\text{so}) = D_+ + D_- ,$$

(20)

$$D_+ = -\frac{7\zeta^2}{20E_1^2}W_2 ,$$

(21)

where we have used so to indicate the crystal-field effect, or, in other words, the spin-orbit coupling mechanism. As can be observed easily, F_+ determines the sign of F in octaheral symmetry $(Dq>0)$ and F_- does so in tetrahedral crystals $(Dq<0)$; a similar case occurs in D. In D_{4h}, W_1 and W_2 are identical in sign, while in D_{2d} they have opposite signs. In the usual case, the term in W_2 is greater in magnitude than that in W_1 for the parameter F. Further, a' behaves as F does. Noting these features we determine the signs of D, F, and a' as follows:

	D	F	a'
Elongated D_{4h}	+	+	−
Compressed D_{4h}	−	−	+
Elongated D_{2d}	−	−	+
Compressed D_{2d}	+	+	−

IV. SIMPLIFIED EXPRESSIONS

The formulas of a' and F derived in Sec. III are considerably tedious. An attempt is made here to simplify them. To do this we note the following.

(i) As can be seen in Tables II and III,

$$F_+^{II}(^4T_2) \approx -\tfrac{1}{2}F_+^{II}(^4E), \quad a_+^{\prime II}(^4T_2) \approx -\tfrac{1}{2}a_+^{\prime II}(^4E) .$$

(ii) The first term of $F_+^{II}(^2T_2)$, $-18\zeta^4 W_2/5E_1^3E_8$, predominates over the remaining parts of $F_+^{II}(^2T_2)$, which are almost canceled by $F_+^{II}(^2E)$. A similar case occurs for a'_+ because of (19). Consequently we have

$$F_+^{II}(^2T_2) + F_+^{II}(^2E) \approx -\frac{18\zeta^4}{5E_1^3E_8}W_2 ,$$

$$a_+^{\prime II}(^2T_2) + a_+^{\prime II}(^2E) \approx \frac{9\zeta^4}{5E_1^3E_8}W_2 .$$

We can also do so because the states $^4T_1(t_2^4(^3T_1)e)$ and $^2T_2(t_2^5)$, having energies E_1 and E_8, respectively, couple most strongly with the ground state ^6S.[15]

(iii) Some terms in the processes of set I involve much smaller numerical coefficients and therefore are negligible.

As the final results we obtain, approximately,

$$F = F(W_1) + F(W_2), \quad a' = a'(W_1) + a'(W_2),$$

(22)

$$F(W_1) = (72W_1\zeta^4/35)\left[\left[\frac{3}{E_1^2E_8^2} - \frac{3}{D_1^2D_8^2}\right] + \left[\frac{1}{E_1} + \frac{1}{E_2}\right]^2\left[\frac{1}{E_6^2} + \frac{1}{E_{14}^2}\right] - \left[\frac{1}{D_1} + \frac{1}{D_2}\right]^2\left[\frac{1}{D_6^2} + \frac{1}{D_{14}^2}\right]\right],$$

(23a)

$$F(W_2) = -(W_2\zeta^4/5)\left[\frac{18}{E_1^3E_8} + \left[\frac{1}{E_1^3} + \frac{1}{E_1^2E_2}\right]\left[\frac{4}{E_4} + \frac{3}{E_5}\right] - \frac{4}{E_1^2E_2E_4}\right.$$

$$\left. - \frac{18}{D_1^3D_8} - \left[\frac{1}{D_1^3} + \frac{1}{D_1^2D_2}\right]\left[\frac{4}{D_4} + \frac{3}{D_5}\right] + \frac{4}{D_1^2D_2D_4}\right],$$

(23b)

$$a'(W_1) = -\tfrac{7}{18}F(W_1),$$

(24a)

$$a'(W_2) = -\tfrac{1}{2}F(W_2) + (6W_2\zeta^4/35)\left[\frac{1}{E_1^2E_8^2} - \frac{1}{D_1^2D_8^2}\right],$$

(24b)

where

$$D_i(Dq) = E_i(Dq \rightarrow -Dq)$$

with E_i listed in Table I. Terms in relation with E_i correspond to F_+ and a'_+, while those in D_i correspond to their complementary parts F_- and a'_-. The expressions fit the self-complementary property (10).

The values of F_+ and a'_+ calculated with the simplified expressions are listed in Tables II and III in comparison with those evaluated with the complete perturbation formulas. The approximation is very good, as can be seen.

The approximation of (19) can be observed plausibly from the simplified expressions. It is noted that $a'(W_2)/F(W_2) \approx -\frac{1}{2}$ holds well because of the negligible value of the last term of (24b). The discrepancy of the ratio $a'/F \equiv -\rho$ from $-\frac{1}{2}$ arises chiefly from the terms related with W_1, for which we have $\rho = 0.39$. More accurately, Eq. (24) predicts

$$0.4 < \rho \lesssim 0.5 \qquad (25a)$$

for the D_{2d} symmetry and

$$\rho \gtrsim 0.5 \qquad (25b)$$

for the D_{4h} symmetry. We have assumed $|F(W_2)| > |F(W_1)|$ in deriving (25b).

V. COMPARISON WITH EXPERIMENTS

A. Mn^{2+} ions in K_2ZnF_4 and K_2MgF_4

The first case we shall consider is Mn^{2+} ions in the D_{4h} crystals K_2ZnF_4 and K_2MgF_4. Although the spin-orbit interaction is weak in Mn^{2+} ions, the rank-four axial term F has been observed[17,18] that is 1 order of magnitude less than the axial rank-two parameter D. The signs of F and D are identical in the crystals, in support of conclusion (v) in Sec. III. They are listed in Table IV together with a. We shall try to understand the crystal-field

TABLE IV. The spin-Hamiltonian parameters of Mn^{2+} ions in K_2ZnF_4 and K_2MgF_4, calculated with $B = 830$ cm^{-1}, $C = 3122$ cm^{-1}, $Dq = 822$ cm^{-1}, $\zeta = 320$ cm^{-1}, $\overline{A}_2 = 4500$ cm^{-1}, $t_2 = 3$, and $t_4 = 7$. All are in 10^{-4} cm^{-1}.

	Mn^{2+}:K_2ZnF_4	Mn^{2+}:K_2MgF_4
R_1 (Å)[a]	2.124±0.015	2.146±0.015
R_2 (Å)[a]	2.072±0.010	2.060±0.012
F (calc)	0.7±0.5	1.2±0.6
F (expt)	1.9±0.6	11±2
a' (calc)	−0.5±0.3	−0.8±0.4
a' (expt)[b]	−0.7±0.2	−4.3±1.0
a (expt)	5.6±0.2	2±1
D(so) (calc)	+322±180	+563±210
D (expt)	+36±0.2	+107±2
References of expt	17	18

[a]Reference 23.
[b]Deduced from experimental values of a and by using $a = a_c + a'$ with $a_c = 6.3 \times 10^{-4}$ cm^{-1} of $KZnF_3$:Mn^{2+} (Ref. 19).

effect on the rank-four splitting parameters with the theory established in the preceding sections.

The crystals have a similar bond length Mn^{2+}—F^- and so a similar cubic crystal field. Thus, one might expect a similar cubic splitting parameter a, without an effect of the low-symmetry field on it. In contrast to the expectation, the values of a have been found to be quite different from each other, as can be seen in Table IV. The low-symmetric-field effect on the cubic term a is not negligible for these crystals.

We assume their cubic crystal fields produce an identical value to a_c, which we take equal to $a = 6.3 \times 10^{-4}$ cm^{-1} of the cubic crystal Mn^{2+}:$KZnF_3$ (Ref. 19), which is identical to that of Mn^{2+}:$KMgF_3$ ($a = 6.5 \pm 0.5 \times 10^{-4}$ cm^{-1}, Ref. 20) in experimental error. The contributions of the low-symmetric fields can thus be estimated: $a' = -0.7 \pm 0.3$ for Mn^{2+}:K_2ZnF_4 and -4.3 ± 1.0 for Mn^{2+}:K_2MgF_4, in units of 10^{-4} cm^{-1}, comparable with the values of a. The deduced a' is opposite in sign to F and D, in support of the conclusion made in Sec. III.

Relationship (19) enables us to estimate F from the deduced values of a'. We obtain $F \approx +1.4 \pm 0.6$ for Mn^{2+}:K_2ZnF_4 (experimental $F = 1.9 \pm 0.6$, Ref. 17) and $+8.6 \pm 2.0$ for Mn^{2+}:K_2MgF_4 (experimental $F = 11 \pm 2$, Ref. 18), in 10^{-4} cm^{-1}. A good agreement is seen between the estimated and the observed values of F.

However, the calculation of an axial parameter suffers from a difficulty owing to the lack of the information about W_1 and W_2. Optical determination of them is actually not practicable because of weak and broad transitions in a $3d^5$ system. Obviously, an available model of crystal fields has to be employed to know their values. As long as Dq is optically obtained together with B and C, W_2 can be reasonably deduced with the use of (17) and (18) of the superposition model. It must be pointed out, however, that one cannot use (20) to deduce W_2 from D, unless he could confirm that the spin-orbit coupling mechanism is most important in the rank-two spin-Hamiltonian parameters. The parameter W_1, or equivalently $\overline{A}_2$ of Eqs. (17) and (18), can only be estimated presumably in the $3d^5$ cases. Finally, and most importantly, in the application of (17) and (18), one has to use the true local structure parameters of an impurity-containing crystal, which may be quite different from those of the host crystal.

It has been found from optical experiments that[21,22] $B = 830$ cm^{-1}, $C = 3122$ cm^{-1}, $Dq = 822$ cm^{-1}, and $\zeta = 320$ cm^{-1} in Mn^{2+}:$KZnF_3$. The parameters result in $a = 6.9 \times 10^{-4}$ cm^{-1} (Ref. 9), in good agreement with the experimental finding 6.3×10^{-4} cm^{-1} (Ref. 19). Using the parameters we obtain, from the simplified expressions,

$$F = 4.4 \times 10^{-7} W_1 - 3.54 \times 10^{-7} W_2 ,$$

$$a' = -1.7 \times 10^{-7} W_1 + 1.83 \times 10^{-7} W_2 ,$$

$$D(\text{so}) = -7.24 \times 10^{-5} W_2 .$$

The local structure of the substitutional crystals has been determined by Barriuso and Moreno.[23] They found from the study of the isotropic superhyperfine constant

TABLE V. The spin-Hamiltonian parameters (10^{-4} cm^{-1}) of Fe^{3+} ions at the tetrahedral sites in garnets, calculated with $B=744$ cm^{-1}, $C=2560$ cm^{-1}, Dq(YGaG)$=-654$ cm^{-1}, $\zeta=420$ cm^{-1}, and $\overline{A}_2$(YGaG)$=8000$ cm^{-1}. Potentials were assumed to be of point charge and structure parameters to remain unchanged from the host lattices.

	YGaG	LuGaG	LuAlG	YAlG
R (Å)[a]	1.85	1.85	1.76	1.76
θ (deg)[a]	49.45	48.90	49.69	49.95
W_1 (cm^{-1})	1225	1355	1355	1287
W_2 (cm^{-1})	-1150	-1230	-1426	-1374
F (calc)	-51	-56	-97	-93
F (expt)[b]	-40	-47	-104	-110
a' (calc)	$+23$	$+24$	$+43$	$+42$
a_c (calc)	$+20$	$+20$	$+42$	$+42$
a (calc)	$+43$	$+44$	$+85$	$+84$
a (expt)[b]	$+62$	$+65$	$+84$	$+75$
D(so) (calc)	-2379	-2192	-3322	-3200
D (expt)[b]	-880	-1131	-1249	-1028

[a]Reference 28.
[b]Reference 26.

A_s that the structure of K$_2$ZnF$_4$ and K$_2$MgF$_4$ changes from compression ($R_1 < R_2$) to elongation ($R_1 > R_2$) when Mn^{2+} impurities are doped in. The values calculated with the use of their results for R_1 and R_2 are displayed in Table IV in comparison with experiments. In the calculation we have presumably taken $\overline{A}_2(R_0)=4500$ cm^{-1}, $R_0=R_1$, $t_2=3$, and $t_4=7$ (Ref. 24). The value of $\overline{A}_2$ is compared to $\overline{A}_2=5500$ cm^{-1} found in the Co^{2+}-Cl$^-$ pair.[25]

The results are good for Mn^{2+}:K$_2$ZnF$_4$ but bad for Mn^{2+}:K$_2$MgF$_4$. Fitting the experimental value of F of Mn^{2+}:K$_2$MgF$_4$ requires $W_2 > 3000$ cm^{-1} and so is impossible according to Barriuso and Moreno. Also, when W_2 reaches such a value, the perturbation procedure we have adopted probably becomes unreliable because it is comparable to $\Delta = 10Dq = 8220$ cm^{-1}. Indeed, the fact that $F \gg a$ implies the complication of the problem. There most probably is another mechanism playing an important role in this case.

It is noted that the obtained values of D(so) are too large to agree with experimental results. This suggests an impossibility of systematic agreement for all the spin-Hamiltonian parameters of the crystals in the crystal-field scheme. Inclusion of other mechanisms is expected to be able to improve the calculated D values.

B. Fe^{3+} ions at the tetrahedral sites in garnets

Fe^{3+} ions at the tetrahedral D_{2d} sites of garnets YGaG, LuGaG, LuAlG, and YAlG provide another good example, indicating the importance of the low-symmetry-field effect on the "cubic" splitting a. Table V lists the comparison between theoretical and experimental values.[26] The results are satisfactory. Especially, the theory predicts the ratio of F of LuAlG and YAlG to that of YGaG and LuGaG to be 1.8, in reasonable agreement with the experimental value 2.5. Furthermore, the

tetragonal fields contribute positive values to a, significantly improving the results in the cubic-field approximation ($a = a_c$).

In the calculation, $B=744$ cm^{-1}, $C=2560$ cm^{-1}, and $Dq=-654$ cm^{-1} found in Fe^{3+}:YGaG were used[27] together with $\zeta=420$ cm^{-1} and $\overline{A}_2$(YGaG)$=8000$ cm^{-1}, and point-charge potentials were assumed that allow $\overline{A}_2 \propto R^{-3}$ and $Dq \propto R^{-5}$. A simple assumption has been taken that the structure remains unchanged when the impurities are doped in, and the x-ray data published by Euler and Bruce[28] have been adopted.

$a' \geq a_c$ indicates the importance of the low-symmetric fields upon the cubic splitting. However, it does not show the fifth order being greater than the fourth order. In fact, the values of a_c were calculated from (9), which is semiempirical and includes contributions not only from the fourth order but from higher orders. The fourth order, according to Yu,[9] gives $a_c^{(4)}=26\times10^{-4}$ cm^{-1}, while the fifth order results in $a_c^{(5)}\approx-6\times10^{-4}$ cm^{-1} for Fe^{3+}:YGaG, for example. Consequently we have

$$a^{(4)}=a_c^{(4)}=26\times10^{-4} \text{ cm}^{-1}$$

and

$$a^{(5)}=a_c^{(5)}+a'=17\times10^{-4} \text{ cm}^{-1} ,$$

so that $a^{(5)} < a^{(4)}$. Actually either W_1 or W_2 is much smaller in magnitude than $\Delta = 10|Dq|$, and therefore it is possible to regard the tetragonal field as a perturbation. Occurring by chance, W_1 and W_2 have positive contributions, unlike the D_{4h} case considered in Sec. V A. Considering the separate contributions of W_1 and W_2, $a'(W_1)$ and $a'(W_2)$, we find each of them considerably smaller than $a^{(4)}$ [for example,

$$a'(W_1)=a'(W_2)=12\times10^{-4} \text{ cm}^{-1} ,$$

compared to $a^{(4)}=26\times10^{-4}$ cm^{-1}, in Fe^{3+}:YGaG] and

see a convergency of the perturbation series.

The calculated $D(\mathrm{so})$ values are 2–3 times greater than the experimental results. A best fitting to the experimental data of D with the spin-orbit coupling model that assumes $D = D(\mathrm{so})$ requires $\zeta = 250$ cm^{-1} (Ref. 12) on the assumption that the local structure around the Fe^{3+} ions is unchanged from the host lattice. Other mechanisms must be taken into account to explain the rank-two axial splitting of the crystals.

There is no regular tetrahedron $(FeO_4)^{5-}$ to allow us to estimate a' from experimental data. Two things we are interested in are that the cubic-field consideration gives results 2–3 times less than the experimental values and that the inclusion of tetragonal fields improves the results remarkably. It has been pointed out that the cubic-field splitting is explicable in terms of the simple crystal-field theory for ionic and regular octahedrally coordinated crystals but is not in strongly covalent-bonded tetrahedral cases for which the covalency effect seems most important compared with the crystal-field effect we are considering. The garnets are ionically bonded and the covalency effect on the "cubic" term a is likely to be small compared with the crystal-field effect.

To know the exact value of ζ is most important in the investigation of the crystal-field effect on the rank-four spin-Hamiltonian parameters as $a \sim \zeta^4$ and $F \sim \zeta^4$. There is no effective way of getting its value in our case. Nevertheless, we believe $\zeta = 250$ cm^{-1} that fit the D data to be unreasonable, because it is too small in comparison with the free-ion value $\zeta_0 = 500$ cm^{-1} (Ref. 29). A rough estimation will show $\zeta = 420$ cm^{-1} to be reliable. Under first approximation we have $B \approx N^4 B_0$ and $\zeta \approx N^2 \zeta_0$ (Refs. 13 and 30), where N denotes the average value of the covalency reduction parameters N_π and N_σ and the subscript 0 refers to the free state. Using $B = 744$ cm^{-1} and $B_0 = 1150$ cm^{-1} we get $\zeta \approx 410$ cm^{-1}, comparable to $\zeta = 420$ cm^{-1} that we have used. Nevertheless, the simple crystal-field model that treats ζ as an adjustable parameter can understand a and F of Fe^{3+} ions at the tetrahedral sites in garnets very well.

VI. SUMMARY

We have studied the crystal-fied effect on the rank-four spin-Hamiltonian parameters of $3d^5$ ions in tetragonal symmetry. Both a and F come chiefly from the fourth-order effect of the spin-orbit interaction among the ground state ^6S and the excited states $^4T_1$, ^4E, $^4T_2$, $^2T_2$, and ^2E. Importantly, the cubic splitting parameter a arises not only from the cubic component of a field, but an additional contribution a' is given by the low-symmetric components and is, in general, not negligible. It has been shown that, roughly, $a' \approx -\frac{1}{2}F$. So one cannot omit the low-symmetric field in the calculation of a, unless F has been found to be negligibly small compared with it.

Neither F nor a can be accurately evaluated by means of diagonalization. A better perturbation procedure may be in treating the low-symmetric field and the spin-orbit coupling as perturbation, as did Blume and Orbach[31] in the calculation of the rank-two parameters. However, the calculation will be considerably complicated, since it requires diagonalization of energy matrices in all excited states. Such a calculation is not expected to change our conclusions.

A crystal field will affect the rank-four terms through the spin-spin interaction and through the spin-orbit coupling via excited configurations $3d^4 4s$, $3d^4 4p$, $3d^4 4d$, etc. The effects, however, are expected to be much smaller compared to what we have considered in this work due to the weakness of the spin-spin interaction and to the much higher energies of the excited configurations. The relativistic effect is also negligible, as has been pointed out by Van Heuvelen.[32] The covalency-overlap effect is likely to be significant and a study of it may be worthwhile.

ACKNOWLEDGMENTS

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