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Analysis of cubic zero-field splitting of Fe^{3+} and Mn^{2+} in tetrahedral coordination

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The *S*-state splitting for high-spin ions Fe^{3+} and Mn^{2+} in tetrahedral coordination has not been satisfactorily interpreted to date. In this paper, a significant coupling mechanism between the ^6S state and the ^4F state has been found. It is shown that a large ground-state splitting for Fe^{3+} and Mn^{2+} in tetrahedral complexes is due to a strong covalency effect.

A theoretical explanation of the d^5 ^6S state splitting in a cubic crystalline field as a very important criterion to check the ligand-field theory has been proposed by Low and Rosengarten.[1–4] Recent works[5–11] show that, for Fe^{3+} and Mn^{2+} in octrahedral coordination, the ground-state splitting can be satisfactorily interpreted by simple crystal-field theory. However, for a d^5-configuration ion in tetrahedral coordination, the calculated values are much smaller than those obtained from experimental data.[9] In this paper, another coupling mechanism between the ^6S state and the ^4F state is reported. We have found that the large cubic zero-field splitting of Fe^{3+} and Mn^{2+} in a tetrahedral ligand field is due to a strong covalency effect.

The spin Hamiltonian for the ^6S-state ion in a cubic ligand field can be written as[26]

$$H_s = -\frac{a}{180}\{O_4^0 + 20\sqrt{2}O_4^3\} \ . \tag{1}$$

The parameter a is associated with a fourth-order spin operator and represents a cubic component of the crystalline electric field. The cubic zero-field splitting for a d^5-configuration ion in the ligand field can be expressed as[1–12]

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

In previous works,[1–12] a strong correlation between the EPR parameter a and the crystal-field strength Dq and the spin-orbit coupling parameter ζ has been reported. In the following we discuss a major contribution due to the covalency effect.

The covalency effect for Fe^{3+} and Mn^{2+} in tetrahedral complexes has been extensively investigated by many workers.[13–18] Deaton, Gebhard, and Solomon[13] remarked that, for a Fe^{3+} ion in $(PPh_4)(FeCl_4)$, the ligand-field independent states $^4E(^4G)$ and $^4E(^4D)$, whose energies depend only upon electron repulsion terms, are found to occur at only 56% and 58% of the energies of the free-ion ^4G term (32 290 cm^{-1}) and ^4D term (38 880 cm^{-1}), respectively. (Here "Ph" is an abbreviation for the phenyl group.) The calculation of Curie, Barthon, and Canny[14] shows that the covalency effect especially for π bonding in a tetrahedral field is much stronger than that of an octahedral field. For example, the normalization parameter for $(MnCl_4)^{2-}$ ($N_t^2 = 0.901$) is much smaller than that of $(MnCl_6)^{4-}$ ($N_t^2 = 0.987$). The covalency effect is associated with the metal d atomic orbitals and the p and s ligand orbitals.

According to molecular-orbital (MO) theory the antibonding d orbitals Ψ_e and Ψ_t for a transition-metal ion in a complex can be written as[19]

$$\begin{aligned} \Psi_e &= (\varphi_e - \lambda_s\chi_s - \lambda_\sigma\chi_\sigma)/N_e^a \ , \\ \Psi_t &= (\varphi_t - \lambda_\pi\chi_\pi)/N_t^a \ , \end{aligned} \tag{3}$$

where

$$(N_e^a)^2 = 1 - 2\lambda_s S_s - 2\lambda_\sigma S_\sigma + \lambda_s^2 + \lambda_\sigma^2 \ ,$$

$$(N_t^a)^2 = 1 - 2\lambda_\pi S_\pi + \lambda_\pi^2 \ .$$

φ_e and φ_t are the metal d atomic orbitals, S_s, S_σ, and S_π are the usual overlap integrals, λ_s, λ_σ, and λ_π are molecular-orbital coefficients, χ_σ, χ_π, and χ_s are the ligand p and s atomic orbitals. Those ligand orbitals would give a contribution to the spin-orbit coupling interaction.

The spin-orbit coupling Hamiltonian for a single electron in a polycentric system is given by Misetich and Buch as[20]

$$H_{\mathrm{s.o.}} = \zeta_0(\mathbf{r}) l \cdot \mathbf{s} + \sum_k \zeta_k(\mathbf{r}_k) l_k \cdot \mathbf{s}_k \ . \tag{4}$$

$\zeta_0(\mathbf{r})$ and $\zeta_k(\mathbf{r}_k)$ are spin-orbit coupling coefficients for the free metal ion and the free ligand ion, respectively. Sugano, Tanabe, and Kamimura[19] indicated that, for a d orbital in a ligand field, there are two spin-orbit coupling parameters ζ and ζ', defined as

$$\begin{aligned} \langle t_2 \| \mathbf{v}(1T_1) \| t_2 \rangle &= 3i\zeta \ , \\ \langle t_2 \| \mathbf{v}(1T_1) \| e \rangle &= -3\sqrt{2}i\zeta' \ , \end{aligned} \tag{5}$$

where $|t_2\rangle$ and $|e\rangle$ are wave functions of the t_2 state and the e state, respectively. The explicit expression for ζ and ζ' can be written as

$$\begin{aligned} \zeta &= (N_t^a)^2(\zeta_d + \tfrac{1}{2}\lambda_\pi^2\zeta_{\mathrm{LP}}) \ , \\ \zeta' &= (N_t^a N_e^a)(\zeta_d - \tfrac{1}{2}\lambda_\pi\lambda_\sigma\zeta_{\mathrm{LP}}) \ , \end{aligned} \tag{6}$$

TABLE I. Cubic zero-field splitting for Fe^{3+} in a tetrahedral field as a function of ζ_2, all in units of cm^{-1}. $B=444$, $C=2728$, $Dq=-655$ for $(FeCl_4)^-$.

ζ_2	$10^4[E_1(\Gamma_8)-E_0(\Gamma_7)]$	$10^4[E_2(\Gamma_8)-E_0(\Gamma_7)]$
0	51.6	51.6
2	87.1	56.4
4	122.8	58.9
6	158.7	59.4
8	194.8	57.8
10	230.8	53.2
12	267.3	46.5
14	303.8	37.6
16	340.5	26.4
20	414.5	−3.1

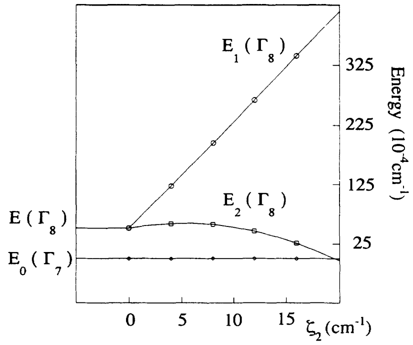

FIG. 1. Cubic zero-field splitting for Fe^{3+} in a tetrahedral field as a function of ζ_2 ($B=444$, $C=2728$, $Dq=-655$, and $\zeta_1=380\ cm^{-1}$).

where ζ_d is the spin-orbit coupling constant for a d electron in a free transition-metal ion, and ζ_{LP} is the spin-orbit coupling constant for a p electron in a free ligand ion. In general the two parameters ζ and ζ' are different. This result is very useful for an understanding of the large ^6S-state splitting for Fe^{3+} and Mn^{2+} in a tetrahedral field.

By utilizing Eq. (5) and basis functions $|J,M_J\rangle$, we have calculated the spin-orbit coupling matrix elements for a d^5 configuration. A significant coupling mechanism between the ^6S state and the ^4F state has been found, which is

$$\begin{aligned}
\langle ^6S,\tfrac{5}{2},\pm\tfrac{1}{2}\|H_{\text{s.o.}}\|^4F,\tfrac{5}{2},\pm\tfrac{1}{2}\rangle &= \frac{6\sqrt{70}}{140}(\zeta-\zeta')\ ,\\
\langle ^6S,\tfrac{5}{2},\pm\tfrac{3}{2}\|H_{\text{s.o.}}\|^4F,\tfrac{5}{2},\pm\tfrac{3}{2}\rangle &= \frac{-9\sqrt{70}}{140}(\zeta-\zeta')\ ,\qquad (7)\\
\langle ^6S,\tfrac{5}{2},\pm\tfrac{5}{2}\|H_{\text{s.o.}}\|^4F,\tfrac{5}{2},\pm\tfrac{5}{2}\rangle &= \frac{3\sqrt{70}}{140}(\zeta-\zeta')\ .
\end{aligned}$$

Obviously, this interaction, which vanishes for a pure d orbital ($\zeta=\zeta'$), is due to the covalency effect. In order to minimize the number of parameters, we take $\zeta_1=(\zeta+\zeta')/2$ and $\zeta_2=(\zeta-\zeta')/2$ and rewrite ζ and ζ' as

$$\zeta=\zeta_1+\zeta_2,\quad \zeta'=\zeta_1-\zeta_2\ . \qquad (8)$$

TABLE II. Cubic zero-field splitting for Mn^{2+} in a tetrahedral field as a function of ζ_2, all in units of cm^{-1}. $B=630$, $C=3040$, $Dq=-600$ for $ZnS:Mn^{2+}$.

ζ_2	$10^4[E_1(\Gamma_8)-E_0(\Gamma_7)]$	$10^4[E_2(\Gamma_8)-E_0(\Gamma_7)]$
0	8.1	8.1
2	22.2	8.8
4	36.4	8.3
6	51.0	5.3
8	65.6	1.3
10	80.6	−4.8

In this work the values ζ_1, $\zeta_1=380\ cm^{-1}$ for Fe^{3+} and $\zeta_1=310\ cm^{-1}$ for Mn^{2+} in tetrahedral fields, are estimated in a reliable range following previous works.[5-12] Taking the same values of the Racah parameters B, C, and the ligand-field strength Dq as those of Deaton, Gebhard, and Solomon[13] ($B=444\ cm^{-1}$, $C=2728\ cm^{-1}$, $Dq=-655\ cm^{-1}$) for Fe^{3+} in $(PPh_4)(FeCl_4)$, and Kushida, Tanaka, and Oka[21] ($B=630\ cm^{-1}$, $C=3040\ cm^{-1}$, $Dq=-600\ cm^{-1}$) for $ZnS:Mn^{2+}$, we obtain the ground-state splittings as a function of parameter ζ_2 by diagonalizing the complete matrix for the ligand field and spin-orbit coupling. The results for Fe^{3+} and Mn^{2+} are listed in Tables I and II respectively. We find three significant results: (1) The covalency effect splits the fourfold state $E(\Gamma_8{:}\cos\alpha|\pm\tfrac{5}{2}\rangle+\sin\alpha|\mp\tfrac{1}{2}\rangle;|\pm\tfrac{3}{2}\rangle)$ into two Kramers states $E_1(\Gamma_8)=E(\Gamma_8{:}\cos\alpha|\pm\tfrac{5}{2}\rangle+\sin\alpha|+\tfrac{1}{2}\rangle)$ and $E_2(\Gamma_8)=E(\Gamma_8{:}|\pm\tfrac{3}{2}\rangle)$. (2) The covalency effect can bring the $E_2(\Gamma_8)$ state close to the twofold state $E_0(\Gamma_7)=E(\Gamma_7{:}\sin\alpha|\pm\tfrac{5}{2}\rangle-\cos\alpha|\mp\tfrac{1}{2}\rangle)$, thus constituting a quartet state, which is at lower energy than that of Kramers doublet state $E_1(\Gamma_8)$. (3) The covalency effect gives rise to a great contribution to zero-field splitting and a linear relationship exists between $E_1(\Gamma_8)-E_0(\Gamma_7)$ and the parameter ζ_2 (for $\zeta_2\le 16\ cm^{-1}$). As shown in Figs. 1 and 2 we have

$$\begin{aligned}
10^4[E_1(\Gamma_8)-E_0(\Gamma_7)] &= 18\zeta_2+51.6\ cm^{-1}\\
&\qquad \text{for } (FeCl_4)^-\ ,\\
10^4[E_1(\Gamma_8)-E_0(\Gamma_7)] &= 7.3\zeta_2+8.1\ cm^{-1} \qquad (9)\\
&\qquad \text{for } ZnS:Mn^{2+}\ .
\end{aligned}$$

Obviously, when the parameter ζ_2 is equal to zero the cal-

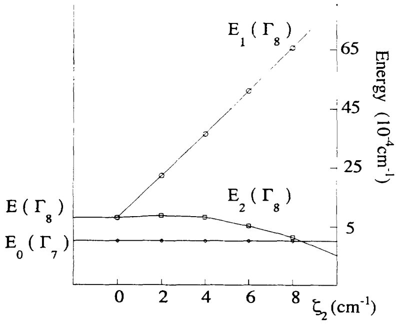

FIG. 2. Cubic zero-field splitting for Mn^{2+} in a tetrahedral field as a function of ζ_2 ($B=630$, $C=3040$, $Dq=-600$, and $\zeta_1=310\ cm^{-1}$).

TABLE III. Comparison between calculated and experimental values of cubic zero-field splitting for Fe^{3+} and Mn^{2+} in a tetrahedral complex, all in units of cm^{-1}.

Complex	Expt. $10^4(3a)$	Calc. $10^4[E_1(\Gamma_8)-E_0(\Gamma_7)]$	$10^4[E_2(\Gamma_8)-E_0(\Gamma_7)]$	ζ_2
$(PPh_4)(FeCl_4)$	255[a]	248.9	50.3	11
YGaG:Fe^{3+}	186[b]	176.4	33.0	11
ZnS:Mn^{2+}	23.7[c]	22.2	2.9	2
Cs_3ZnCl_5:Mn^{2+}	32.1[d]	31.6	−20.3	12

[a] See Ref. 13.
[b] See Ref. 23.
[c] See Ref. 25.
[d] See Ref. 22.

culated values of splitting, 51.6×10^{-4} cm,$^{-1}$ for $(FeCl_4)^-$ and 8.1×10^{-4} cm^{-1} for ZnS:Mn^{2+}, are much smaller than those of the experimental data ($3a$), 255×10^{-4} cm^{-1} for $(FeCl_4)^-$ and 23.7×10^{-4} cm^{-1} for ZnS:Mn^{2+}. A reasonable fit between $10^4[E_1(\Gamma_8)-E_0(\Gamma_7)]$ and $10^4(3a)$ for $(PPh_4)(FeCl_4)$, and ZnS:Mn^{2+} can be found by ζ_2 equal to 11 cm^{-1} and 2 cm^{-1}, respectively. Similarly, from the EPR and optical experimental data of Fe^{3+} in YGaG [$B=744$ cm^{-1}, $C=2560$ cm^{-1}, $Dq=-654$ cm^{-1}, and $10^4(3a)=186$ cm^{-1}] (Refs. 10 and 23) and Mn^{2+} in Cs_3ZnCl_5 ($B=558$ cm^{-1}, $C=3524$ cm^{-1}, $Dq=-360$ cm^{-1}, and $10^4(3a)=32.1$ cm^{-1} (Refs. 24 and 25), we obtain the parameter ζ_2 equal to 11 cm^{-1} and 12 cm^{-1}, respectively (see Table III). This implies that the covalency effect is very important for understanding the large ^6S-state splitting of high-spin ions Fe^{3+} and Mn^{2+} in a tetrahedral ligand field.

We can draw the following conclusions: (1) In general, a significant spin-orbit coupling mechanism exists between the ^6S state and the ^4F state; this gives rise to a major contribution to the ground-state splitting for d^5-configuration ions in the ligand field. (2) The large cubic zero-field splitting for Fe^{3+} and Mn^{2+} in a tetrahedral ligand field is due to a strong covalency effect.

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