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Quantum-Admixture Model of High-Spin ↔ Low-Spin Transition for Ferrous Complex Molecules

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A quantum-admixture model for the d^6 configuration ferrous complex molecules with the high-spin ↔ low-spin transition has been established by using the unified crystal-field-coupling (UCFC) scheme. A general study has been made on the spin transition of octahedrally coordinated d^6 complexes, and a special application has been given to an Fe(II) compound $Fe^{II}(TRIM)_2(PhCO_2)(ClO_4)$. The results show the following: (i) The quantum picture of the spin transition of a d^6 system, such as Fe(II), is much more complex than a simple transition between the pure $^5T_{2g}$ and $^1A_{1g}$ states as usually understood. In practice, owing to spin−orbit coupling, spin is no longer a good quantum number and there is no longer a pure $^5T_{2g}$ or $^1A_{1g}$ state. Each of them splits into substates and each substate is a linear combination of various multiplets. The high-spin → low-spin transition of an octahedrally coordinated d^6 ion is practically the crossover of the two lowest substates of $^5T_{2g}$ at the critical point. (ii) At the spin-transition critical point the magnetic moment $\mu_{\mathrm{eff}} \approx 5.22\mu_B$, which is obviously different from the simple average of the μ_{eff} values of high-spin and low-spin states but near the saturation value. (iii) The calculation of the effective molecular magnetic moment μ_{eff} for an octahedrally coordinated Fe(II) ion shows that the $\mu_{\mathrm{eff}}-T$ curve is in good agreement with Lemercier et al.'s experiment and both the low-spin value $\mu_{\mathrm{eff}} = 0.51\mu_B$ and the high-spin value $\mu_{\mathrm{eff}} = 5.4\mu_B$ are comparable with the experimental values $0.76\mu_B$ and $5.4\mu_B$, respectively. (iv) The T dependence of the crystal field parameter Dq in the spin-transition region is approximately linear.

I. Introduction

The ferrous molecules with spin-transition effects, which have received considerable attention in the past decade, are found in chemical and biochemical systems. This spin-transition phenomenon arises when the ligand-field splitting energy becomes comparable with the mean spin pairing energy. At the molecular scale, it is possible to understand the spin transition as an intraionic transfer with spin flip of the transferred electrons. For the ferrous molecules this transfer, depending on the coordination and distortion of the molecules, may involve either two electrons or one electron, the former being associated with the high-spin ↔ low-spin (HS ↔ LS) transition and having $\Delta S = 2$, and the latter with the high-spin ↔ intermediate-spin transition or the intermediate-spin ↔ low-spin transition and having $\Delta S = 1$.[1−12] To reproduce the spin transition, several physical models, such as the spin-equilibrium model,[13] the thermodynamical models,[14−16] the Ising-like models,[17−19] the vibronic models,[20,21] and the quantum-admixture models,[22−25] have been proposed and some great progresses have been made. However, due to the limitation of the weak-field scheme, the quantum-admixture model for d^6 configuration ferrous molecules with HS ↔ LS transition has not yet been established and up to now, the physical mechanism and the main interactions that govern the HS ↔ LS transition in ferrous molecules have not yet been determined.

To understand the physical origin and to determine the main mechanism of the HS ↔ LS transition, chemists have synthesized a number of model complexes. Among those, an especially important one is the $Fe^{II}(TRIM)_2(PhCO_2)(ClO_4)$, which is prepared by Lemercier et al.[1] This interesting model complex displays a gradual $^5T_{2g}$ ↔ $^1A_{1g}$ spin-state conversion and shows that the effective magnetic moments μ_{eff} in the LS and HS states are respectively $0.76\mu_B$ and $5.4\mu_B$, being evidently larger than those usually evaluated by the Curie formula $\mu_{\mathrm{eff}}^2 = \mu_B^2 g_s^2 S(S + 1)$, i.e., 0 and $4.9\mu_B$. Lemercier et al. have explained this difference by supposing the existence of some Fe(III) impurity. However, this viewpoint is not confirmed and the μ_{eff} of all octahedral HS complexes that we know is larger evidently than $4.9\mu_B$. A greater challenge that faces the theoretical works is that, owing to spin−orbit (S−O) coupling, each multiplet of an Fe(II) ion is split into substates and each substate is a linear combination of multiplets with different spin and different symmetry, then spin is no longer a good quantum number and there is no pure $^5T_{2g}$ and $^1A_{1g}$ states. Therefore, it is not appropriate to regard the spin transition of Fe(II) complex molecules as a simple transition between $^5T_{2g}$ and $^1A_{1g}$. Up to now there is no microscopic theory that can be used to reveal how the electronic structure and molecular magnetic property of a d^6 configuration ion in a ligand field changes in a HS ↔ LS spin transition. There is also no reasonable quantum explanation about the Lemercier et al.'s experimental result.[1]

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In present work, using the unified crystal-field-coupling (UCFC) scheme crystal field theory,[26] we will develop a quantum theory based upon a concept of standard basis and standard energy matrix for the electronic structure of 3d^n (n = 4, 6) compounds. By this theory we will calculate the electronic structure, the molecular magnetic moment, and the multiplet structure of the quantum states of a general octahedrally coordinated d^6 ion and study how these change in a HS ↔ LS spin transition. From this theory a detailed description will be made for the spin-transition course. Again, an interpretation will be given for Lemercier et al.'s experiment. In the second part of the paper, we will introduce the Hamiltonian and construct for the first time the standard basis in the spin−orbit coupling representation of the d^6 configuration space and the corresponding standard complete energy matrix of an octahedrally coordinated d^6 ion. It should be emphasized that although the concept of standard basis was introduced by Griffith[27] for the irreducible representations of the point groups, our standard basis is defined for the whole d^6 configuration space. The dimension of the former is only 1−4, whereas that of the latter is 210. Owing to the special structure of our standard basis, each eigenvector of the standard energy matrix carries evidently the information about spin and space symmetry. Only with this we can describe the change of state in spin-transition course. In the third and fourth parts, we will calculate the energy levels, states, and the molecular magnetic moment and describe how they change in the spin-transition course.

II. From d^4(O_h) Standard Basis to d^6(O_h^*) Standard Energy Matrix

The Hamiltonian of the d^n electron configuration of a transition metal ion in a ligand field (or named crystal field) can be written as[27]

$$\mathscr{H} = \sum_{\kappa=1}^{n}\left\{\frac{1}{2m}\mathbf{p}_\kappa^{\,2} - \frac{Ze^2}{r_\kappa} + \xi(r_\kappa)\mathbf{l}_\kappa\cdot\mathbf{s}_\kappa + V(\mathbf{r}_\kappa)\right\} + \sum_{\kappa<\lambda}^{n}\frac{e^2}{r_\kappa\lambda}$$

In a cubic crystal field it can be simplified as the following parametrized form:

$$\mathscr{H} = \mathscr{H}^0 + \mathscr{H}^{ee}(B,C) + V^{A_1}(Dq) + \mathscr{H}^{so}(\zeta) \qquad (1)$$

where $\mathscr{H}^0$ is the effective center potential, $\mathscr{H}^{ee}(B,C)$ is the electrostatic interaction between the d-electrons, B and C are the Racah parameters, $V^{A_1}(Dq)$ is the cubic crystal field energy of the d-electrons, Dq is the crystal field intensity parameter (also named crystal field intensity), $\mathscr{H}^{so}(\zeta)$ is the S−O coupling energy, and ζ is the S−O coupling parameter. When an applied magnetic field exists, the following Zeeman energy should be added to the Hamiltonian,[27]

$$\mathscr{H}^{Zeeman} = \mu_B\hat{H}\cdot(\hat{L} + g_s\hat{S}) \qquad (2)$$

where μ_B is the Bohr magneton, $g_s = 2.0023$.

Let O_h stand for the octahedral group and O_h^* the corresponding double group. Hereafter we will use d^n(O_h^*) to denote an octahedrally coordinated d^n system with S−O coupling, being described in a S−O coupling representation, and d^n(O_h) to denote the same system but without S−O coupling, being described in an uncoupling representation.

To ensure each eigenvector of the matrix of a d^n system should contain evidently the information about the spin multiplicity and space symmetry, we will construct the energy matrix of the Hamiltonian in the standard basis defined according to the UCFC theory.[26] It is well-known that for an energy matrix of a d^4 system, if its parameters Dq and ζ are replaced respectively by $-Dq$ and $-\zeta$, it will be changed into a d^6 matrix. Therefore we need only constructing the d^4(O_h) and d^4(O_h^*) matrices. For this, we will first construct a standard basis of a d^4(O_h) system, and then, by linear combinations of its components, construct a standard basis of a d^4(O_h^*) system, in which we then construct the standard d^4(O_h^*) energy matrix. Due to the special structure of these standard bases, the d^4(O_h^*) matrix, when S−O coupling is omitted, will be a block diagonal form with blocks cut from the d^4(O_h) matrix. Finally, the d^4(O_h^*) matrix, when its parameters Dq and ζ are replaced respectively by $-Dq$ and $-\zeta$, will become the standard complete energy matrix of a d^6(O_h^*) system.

1. Standard Basis and Energy Matrix of a d^4(O_h) System. In constructing the wave functions of a multielectron system, the standard d-electron wave functions θ, ϵ, ξ, η, ζ, also named d orbitals, that have been defined by Grifith[27] will be adopted. An octahedral crystal field separates the d orbitals into two sets, e$_g$(θ,ϵ) and t$_{2g}$(ξ,η,ζ), the energy space between them is usually determined as 10Dq. From any four d orbitals d$_{k1}$, d$_{k2}$, ..., d$_{k4}$ we can construct a Slater type determinant wave function, denoted by |d$_{k1}$d$_{k2}$...d$_{k4}$|. Such Slater functions are orthonormal and satisfy the requirement of antisymmetry of the Pauli principle, and by their linear combinations we can obtain all wave functions of the d^4 electron configuration. All these functions can be divided into sets according to the t$_{2g}$-electron number m and the e$_g$-electron number n. Each set is called a strong-field configuration and is denoted by t$_2{}^m$e^n. The electrostatic interaction between the d-electrons separates the quantum states belonging to a t$_2{}^m$e^n configuration into subgsets; each subgset has a definite spin S and belongs to a definite irreducible representation Γ of the octahedral group O_h. The whole of the states of a subset is called a crystal-field term, denoted by $S\Gamma$ or $^{2S+1}\Gamma$. The terms permitted for a d^4(O_h) system, as well as a ^{6}(O_h) system, are listed below according to a definite order and with their suffix g omitted:

$$^5E,\ ^5T_2,\ ^3A_1,\ ^3A_2,\ ^3E,\ ^3T_1,\ ^3T_2,\ ^1A_1,\ ^1A_2,\ ^1E,\ ^1T_1,\ ^1T_2 \qquad (3)$$

Each term can include states, which can be distinguished by the strong-field configuration that they belong to. Of each term the states will be numbered according to the order defined by Griffith.[27] The $S\Gamma$ terms of the special strong-field configurations t$_{2g}{}^m$ and e$_g{}^n$ have been given by Griffith.[27] Of these $S\Gamma$ terms the wave functions of all the states having $M = S$ have been given in the $S\Gamma M\gamma$ quantization representation (M is the spin magnetic quantum number, γ the real component of Γ).[27] These special strong-field term wave functions are denoted respectively as $|t_2{}^m(S\Gamma M\gamma)\rangle$ and $|e^n(S\Gamma M\gamma)\rangle$; each is a linear combination of Slater functions. With these functions we can construct strong-field term wave functions $|t_2{}^m(S_1\Gamma_1)e^n(S_2\Gamma_2)S\Gamma M\gamma\rangle$ of all general terms t$_2{}^m$e^n by the following formula,

$$|t_2{}^m(S_1\Gamma_1)e^n(S_2\Gamma_2),S\Gamma M\gamma\rangle = \sum_{M_1M_2}\langle S_1S_2M_1M_2|SM\rangle\sum_{\gamma_1\gamma_2}\langle\Gamma_1\Gamma_2\gamma_1\gamma_2|\Gamma\gamma\rangle\cdot |t_2{}^m(S_1\Gamma_1M_1\gamma_1)\rangle\otimes|e^n(S_2\Gamma_2M_2\gamma_2)\rangle \qquad (4)$$

The notations $\langle S_1S_2M_1M_2|SM\rangle$ and $\langle\Gamma_1\Gamma_2\gamma_1\gamma_2|\Gamma\gamma\rangle$ are respectively the Wigner and CG coefficients given by Griffith.[27] Γ is generated by coupling Γ_1 and Γ_2, and M is generated by coupling M_1 and M_2, requiring $M_1 + M_2 = M$. Between the states

$|\mathrm{t}_2^m(S\Gamma M\gamma)\rangle$ and $|\mathrm{e}^n(S\Gamma M\gamma)\rangle$ in (4) we defined a special multiplication, denoted by the operator $\otimes$ and named "direct multiplication", to overcome the difficulties in antisymmetrizing the product functions by usual multiplication. Direct multiplication generates a $(m + n) \times (m + n)$ Slater determinant from an $m \times m$ and an $n \times n$ Slater determinant according to the following formula,

$$|d_{k1}d_{k2} \cdots d_{km}| \otimes |d_{p1}d_{p2} \cdots d_{pn}| = |d_{k1}d_{k2} \cdots d_{km}d_{p1}d_{p2} \cdots d_{pn}|$$

It is automatically antisymmetric. For example, we have $|\zeta^+\zeta^-\eta^+| \times |\theta^+\epsilon^-| = |\zeta^+\zeta^-\eta^+\theta^+\epsilon^-|$. As a stipulation we write first the t and then the e electrons in a determinant.

We define such an ordered set formed by the 210 strong-field term wave functions (4) as the standard basis of a $\mathrm{d}^4(O_h)$ system. Each function is a component of this basis and thus we call it a basis function. In this basis the electrostatic matrix is a block diagonal form. Each block belongs to a definite $S\Gamma$ term and we call it the $S\Gamma$ block. Such blocks are degenerate for M and γ. The $S\Gamma$ blocks are the same as that given by Griffith.[27] The crystal field matrix is an entirely diagonalized form, of which the diagonal elements are calculated by the following formula,

$$\langle \mathrm{t}_2{}^m\mathrm{e}^n,S\Gamma M\gamma|V^{\mathrm{A}_1}|\mathrm{t}_2{}^m\mathrm{e}^n,S\Gamma M\gamma\rangle = (6n - 4m)Dq \qquad (5)$$

Then we have obtained the $\mathrm{d}^4(O_h)$ standard energy matrix of $\mathscr{H}^{\mathrm{ee}}(B,C) + V^{\mathrm{A}_1}(Dq)$. It is also an $S\Gamma$ block diagonal form and each block is the electrostatic $S\Gamma$ block if the corresponding crystal field elements (5) are added on the diagonal of the latter.

2. Standard Basis of a $\mathbf{d^4(O_h^*)}$ System. Now we consider the S−O coupling of a state described by a strong-field term wave function in (4), which can be abbreviated as $|q,S\Gamma M\gamma\rangle$, where q stands for the strong-field configuration $\mathrm{t}_2{}^m(S_1\Gamma_1)\mathrm{e}^n(S_2\Gamma_2)$. In general, $|q,S\Gamma M\gamma\rangle$ cannot be written as a form having its space and spin separated, as $|q,\Gamma\gamma\rangle|SM\rangle$. However, under a rotation of the spin space and/or a point-symmetric operation in the coordinate space, the behavior of the two forms is exactly the same. Therefore, in any treatment based on pure group theory, $|q,S\Gamma M\gamma\rangle$ can be replaced by $|q,\Gamma\gamma\rangle|SM\rangle$ and again $|q,\Gamma\gamma\rangle$ can be replaced by $|q,\mathring{S}\Gamma\mathring{M}\gamma\rangle$, which is the function $|q,S\Gamma M\gamma\rangle$ but having its spin frozen and $M = S$. With the word "frozen" we mean that the function cannot be operated by any spin operator or/and group element in spin space. Now consider the spin states $|SM\rangle$. With these states we can obtain a set of symmetrically matched standard basis functions $|\tilde{\Gamma}\tilde{\gamma}\rangle$ according to the formula

$$|\tilde{\Gamma}\tilde{\gamma}\rangle = \sum_M \langle SM|\tilde{\Gamma}\tilde{\gamma}\rangle|SM\rangle \qquad (6)$$

It forms the γ component of the irreducible representation Γ of O_h^*. These functions are

S	$\tilde{\Gamma}\tilde{\gamma}$
0	$\mathrm{A}_1\mathrm{a}_1 = \|0,0>$
1	$T_1x = (i/\sqrt{2})(T_11 - T_1 - 1) = (i/\sqrt{2})(\|11\rangle - \|1 - 1\rangle)$
	$T_1y = (1/\sqrt{2})(T_11 + T_1 - 1) = (1/\sqrt{2})(\|11\rangle + \|1 - 1\rangle)$
	$T_1z = -iT_10 = -\, i\|10\rangle$
2	$E\theta = \|20\rangle$
	$E\epsilon = (1/\sqrt{2})(\|22\rangle + \|2 - 2\rangle)$
	$T_2\xi = (i/\sqrt{2})(T_21 - T_2 - 1) = (i/\sqrt{2})(\|2 - 1\rangle + \|21\rangle)$
	$T_2\eta = (1/\sqrt{2})(T_21 + T_2 - 1) = (1/\sqrt{2})(\|2 - 1\rangle - \|21\rangle)$
	$T_2\zeta = -iT_20 = -\,(i/\sqrt{2})(\|22\rangle - \|2 - 2\rangle)$

Therefore we have

$$|SM\rangle = \sum_{\tilde{\Gamma}\tilde{\gamma}} \langle\tilde{\Gamma}\tilde{\gamma}|SM\rangle|\tilde{\Gamma}\tilde{\gamma}\rangle \qquad (7)$$

Then, in any treatment based on pure group theory, we will apply the following replacement,

$$|q,\mathring{S}\Gamma\mathring{M}\gamma\rangle|\tilde{\Gamma}\tilde{\gamma}\rangle \rightarrow |q,S\Gamma M\gamma\rangle$$

Obviously, for any q_i, the whole of the following product functions forms a representation of the direct product $\Gamma \times \tilde{\Gamma}$,

$$|q_i,\mathring{S}\Gamma\mathring{M}\gamma\rangle|\tilde{\Gamma}\tilde{\gamma}\rangle \qquad (8)$$

In the O_h^* group $\Gamma \times \tilde{\Gamma}$ can be reduced into irreducible representations, denoted by Γ':

$$\Gamma \times \tilde{\Gamma} = \sum \beta\Gamma' \qquad (9)$$

where β is used to distinguish the repeated Γ's. It can be seen from (9) that the basis functions of $\Gamma'(O_h^*)$ can be formed by linear combinations of the product functions in (8). For any q_i we write such a basis function as $|q_i,S\Gamma\tilde{\Gamma}\beta\Gamma'\gamma'\rangle$ and we have

$$|q_i,S\Gamma\tilde{\Gamma}\beta\Gamma'\gamma'\rangle = \sum_{\gamma\tilde{\gamma}} \langle\Gamma\gamma\tilde{\Gamma}\tilde{\gamma}|\beta\Gamma'\gamma'\rangle|q_i,\mathring{S}\Gamma\mathring{M}\gamma\rangle|\tilde{\Gamma}\tilde{\gamma}\rangle \qquad (10)$$

where $\langle\Gamma\gamma\tilde{\Gamma}\tilde{\gamma}|\beta\Gamma'\gamma'\rangle$ is the CG coefficient corresponding to $\Gamma \times \tilde{\Gamma} \rightarrow \beta\Gamma'$. (10) gives a set of 210 S−O coupling states (whereas the states in (4) are uncoupling states). It is a linearly independent and complete function set, which forms a representation of the d^4 electron configuration space, named S−O coupling representation or $S\Gamma\tilde{\Gamma}\beta\Gamma'\gamma'$ quantization representation. Therefore the 210 functions in (10) are the $\mathrm{d}^4(O_h^*)$ basis functions; in constructing them, only the $\mathrm{d}^4(O_h)$ basis functions with $M = S$ are needed and the others need not be known.

We divide the $\mathrm{d}^4(O_h^*)$ basis functions into 10 sets according to different $\Gamma'\gamma'$. Each set is called a $\Gamma'\gamma'$ term. They are listed according to a definite order as follows,

$$A_1'(14),\ A_2'(8),\ E'\theta(19),\ E'\epsilon(19),\ T_1'x(23),\ T_1'y(23),\ T_1'z(23),\ T_2'\xi(27),\ T_2'\eta(27),\ T_2'\zeta(27) \qquad (11)$$

In the parentheses after a term symbol is the number of basis functions belonging to that term. We number the functions in each $\Gamma'\gamma'$ term according to the order S, Γ, $\tilde{\Gamma}$, q and define such an ordered set of the 210 functions as the standard basis of a $\mathrm{d}^4(O_h^*)$ system.

3. Standard Energy Matrices of $\mathbf{d^4(O_h^*)}$ and $\mathbf{d^6(O_h^*)}$ Systems. The matrix of Hamiltonian (1) constructed in the $\mathrm{d}^4(O_h^*)$ standard basis is called $\mathrm{d}^4(O_h^*)$ standard matrix. Because Hamiltonian (1) belongs to the representation A_1 of O_h^*, this matrix is a block diagonal form and each block belongs to a definite $\Gamma'\gamma'$ term; thus we denote it also by $\Gamma'\gamma'$. Then the symbols in (11) represent also such ten blocks. The blocks with the same Γ' are identical. The complete matrix is a sum of the matrices of all operators included in the Hamiltonian; therefore we need only construct respectively the matrix of each operator in the $\mathrm{d}^4(O_h^*)$ standard basis, as will be done below.

(1) Matrix of $\mathscr{H}^{\mathrm{ee}}(B,C) + V^{A_1}(Dq)$. Obviously this matrix is also a block diagonal form with 10 $\Gamma'\gamma'$ blocks, each is again a block diagonal form with some $S\Gamma$ blocks cut from the $\mathrm{d}^4(O_h)$ standard matrix.

(2) Matrix of $\mathscr{H}^{\mathrm{so}}(\zeta)$. Obviously this matrix is also a diagonal form with 10 $\Gamma'\gamma'$ blocks. Each $\Gamma'\gamma'$ block can be divided into

$S\Gamma$ blocks. Each $S\Gamma$ block belongs to two $S\Gamma$ terms, e.g., $S_1\Gamma_1$ and $S_2\Gamma_2$. The elements in a $S\Gamma$ block can again be divided into $\tilde{\Gamma}\beta$ blocks. Each $\tilde{\Gamma}\beta$ block belongs to two $\tilde{\Gamma}\beta$. The (i,j)th element in a $\tilde{\Gamma}\beta$ block can be calculated with the following formula,

$$\begin{aligned}
&\mathscr{H}_{ij}^{\mathrm{so}}(\Gamma',S_1\Gamma_1\tilde{\Gamma}_1\beta_1,S_2\Gamma_2\tilde{\Gamma}_2\beta_2)\\
&\equiv \langle q_iS_1\Gamma_1\tilde{\Gamma}_1\beta_1\Gamma'\gamma'|\mathscr{H}^{\mathrm{so}}|q_jS_2\Gamma_2\tilde{\Gamma}_2\beta_2\Gamma'\gamma'\rangle\\
&= \langle q_i,S_1\Gamma_1\tilde{\Gamma}_1\beta_1\Gamma'\gamma'|\sum_{\gamma^*=-1}^{+1} V^{1T_1}_{\gamma^*-\gamma^*}(-1)^{1+\gamma^*}|q_j,S_2\Gamma_2\tilde{\Gamma}_2\beta_2\Gamma'\gamma'\rangle\\
&= \sum_{\gamma_1\tilde{\gamma}_1\gamma_2\tilde{\gamma}_2}[\langle\Gamma_1\gamma_1\tilde{\Gamma}_1\tilde{\gamma}_1|\beta_1\Gamma'\gamma'\rangle\langle\Gamma_2\gamma_2\tilde{\Gamma}_2\tilde{\gamma}_2|\beta_2\Gamma'\gamma'\rangle\cdot\\
&\qquad\qquad \sum_{M_1M_2}\langle\tilde{\Gamma}_1\tilde{\gamma}_1|S_1M_1\rangle\langle S_2M_2|\tilde{\Gamma}_2\tilde{\gamma}_2\rangle\cdot\\
&\quad \sum_{\gamma^*=-1}^{1}(-1)^{1+\gamma^*}\langle S_1M_1|\langle q_i,\mathring{S}_1\Gamma_1\mathring{M}_1\gamma_1|V^{1T_1}_{\gamma^*-\gamma^*}|q_j,\mathring{S}_2\Gamma_2\mathring{M}_2\gamma_2\rangle|S_2M_2\rangle]\\
&= K'\,\langle q_iS_1\Gamma_1||V^{1T_1}||q_jS_2\Gamma_2\rangle
\end{aligned}\tag{12}$$

where K' is the transfer coefficient. We have

$$\begin{aligned}
&K' \equiv K'(\Gamma',S_1\Gamma_1\tilde{\Gamma}_1\beta_1S_2\Gamma_2\tilde{\Gamma}_2\beta_2)\\
&\quad = \sum_{\gamma_1\gamma_2M_1M_2}\Bigg[\frac{1}{\sqrt{(2S_1+1)\lambda(\Gamma_1)}}\cdot\\
&\sum_{\tilde{\gamma}_1}\langle\tilde{\Gamma}_1\tilde{\gamma}_1|S_1M_1\rangle\langle\Gamma_1\gamma_1\tilde{\Gamma}_1\tilde{\gamma}_1|\beta_1\Gamma'\gamma'\rangle\sum_{\tilde{\gamma}_2}\langle S_2M_2|\tilde{\Gamma}_2\tilde{\gamma}_2\rangle\langle\Gamma_2\gamma_2\tilde{\Gamma}_2\tilde{\gamma}_2|\beta_2\Gamma'\gamma'\rangle\cdot\\
&\qquad\qquad \sum_{\gamma^*=1}^{-1}(-1)^{1+\gamma^*}\cdot\langle S_1M_1|S_2M_21\gamma^*\rangle\langle\Gamma_1\gamma_1|\Gamma_2\gamma_2T_1-\gamma^*\rangle\Bigg]
\end{aligned}\tag{13}$$

Except $S_1 = S_2 = 0$ the reduced matrix elements $\langle q_iS_1\Gamma_1||V^{1\mathrm{T}_1}||q_jS_2\Gamma_2\rangle$ in (12) can be calculated with the following formula,

$$\begin{aligned}
&\langle q_iS_1\Gamma_1||V^{1T_1}||q_jS_2\Gamma_2\rangle =\\
&\qquad \frac{(-1)^{S_2-S_1-1}\sqrt{(2S_1+1)\,\dim(\Gamma_1)}}{\langle S_2M_21\gamma|S_1M_1\rangle\langle\Gamma_2\gamma_2T_1-\gamma^*|\Gamma_1\gamma_1\rangle}\cdot\\
&\qquad\qquad \langle q_iS_1\Gamma_1M_1\gamma_1|\mathscr{H}^{\mathrm{so}}|q_jS_2\Gamma_2M_2\gamma_2\rangle
\end{aligned}\tag{14}$$

where $M_1 \equiv S_1$, $M_2 \equiv S_2$, and $\gamma^* \equiv S_1 - S_2$, $\dim(\Gamma)$ is the dimension of Γ, γ_1 and γ_2 can be selected arbitrarily as long as the CG coefficient $\langle\Gamma_2\gamma_2T_1 - \gamma^*|\Gamma_1\gamma_1\rangle \neq 0$. When $S_1 = S_2 = 0$, we have $K' = 0$; thus the corresponding reduced matrix elements need not be known.

To ensure the S−O matrix element between two basis functions, e.g., f_1 and f_2, does not vanish, the necessary condition in the S−O coupling representation is that f_1 and f_2 belong to the same $\Gamma'\gamma'$; in the uncoupling representation the condition is that $S_1 - S_2 = \pm 1$ *or* 0 and $T_1 \in \Gamma_1 \times \Gamma_2$.

(3) Zeeman Energy Matrix. To establish the Zeeman energy matrix, we need only establish the matrices of the angular momentums.

(a) Matrix of Spin Angular Momentum. The matrix of a spin operator $S\bar{\gamma}$ ($\bar{\gamma} = x, y, z, 1, 0, -1, +, -$) constructed in the $d^4(O_h^*)$ standard basis can be divided in to blocks according to each $\Gamma'\gamma'$ pair. The elements in each $\Gamma'\gamma'$ block can be divided into subblocks according to each $S\Gamma\tilde{\Gamma}$ pair. Such $S\Gamma\tilde{\Gamma}$ subblocks are diagonal for $S\Gamma$ and depend on $\tilde{\Gamma}$, and the elements in each are diagonal and degenerate for q. Therefore only the elements in each $S\Gamma$ term cannot be zero; those can be calculated by the following formula:

$$\begin{aligned}
[S_{\bar{\gamma}}]_{ij} &= \langle qS\Gamma\tilde{\Gamma}_1\beta_i\Gamma'_1\gamma'_1|S\bar{\gamma}|qS\Gamma\tilde{\Gamma}_2\beta_j\Gamma'_2\gamma'_2\rangle\\
&= \sum_{\gamma\tilde{\gamma}_1\tilde{\gamma}_2}\langle\Gamma\gamma\tilde{\Gamma}_1\tilde{\gamma}_1|\beta_i\Gamma'_1\gamma'_1\rangle\langle\Gamma\gamma\tilde{\Gamma}_2\tilde{\gamma}_2|\beta_j\Gamma_2{}'\gamma_2{}'\rangle\\
&\qquad\qquad \langle\tilde{\Gamma}_1\tilde{\gamma}_1|\langle q\mathring{S}\Gamma\mathring{M}\gamma|S\bar{\gamma}|q\mathring{S}\Gamma\mathring{M}\gamma\rangle|\tilde{\Gamma}_2\tilde{\gamma}_2\rangle\\
&= \sum_{\gamma\tilde{\gamma}_1\tilde{\gamma}_2}\langle\Gamma\gamma\tilde{\Gamma}_1\tilde{\gamma}_1|\beta_i\Gamma'_1\gamma'_1\rangle\langle\Gamma\gamma\tilde{\Gamma}_2\tilde{\gamma}_2|\beta_j\Gamma'_2\gamma'_2\rangle\langle\tilde{\Gamma}_1\tilde{\gamma}_1|S_{\bar{\gamma}}|\tilde{\Gamma}_2\tilde{\gamma}_2\rangle
\end{aligned}\tag{15}$$

(b) Matrix of Orbital Angular Momentum. Because each basis function is a linear combination of Slater determinants, the *m*th basis function can be written as

$$f_m = \sum_{k=l}^{N_m} R_{m,k}W_{m,k}$$

where $W_{m,k}$ is the *k*th determinant, $R_{m,k}$ is its coefficient, N_m is the number of determinants. Then the matrix element of an orbital angular momentum $L_{\bar{\gamma}} = \sum l_{\bar{\gamma}}$ ($\bar{\gamma} = x, y, z$) between f_m and f_n can be written as a linear combination of single electron matrix elements $\langle d_i|l_{\bar{\gamma}}|d_j\rangle$:

$$\begin{aligned}
L_{\bar{\gamma}}(m,n) = \langle f_m|L_{\bar{\gamma}}|f_n\rangle &= \sum_{k=1}^{N_m}\sum_{l=1}^{N_n} R_{m,k}R_{n,l}\langle W_{m,k}|L_{\bar{\gamma}}|W_{n,l}\rangle\\
&= \sum_{i,j=1}^{10} b_{ij}(m,n)\langle d_i|l_{\bar{\gamma}}|d_j\rangle
\end{aligned}\tag{16}$$

where d_i is the *i*th orbital in the d orbital series (θ, ϵ, ξ, η, ζ, $\bar{\theta}$, $\bar{\epsilon}$, $\bar{\xi}$, $\bar{\eta}$, $\bar{\zeta}$) and $b_{ij}(m,n)$ is the combination coefficient.

The standard complete energy matrix of a $d^4(O_h^*)$ system is the sum of the above matrices. When the parameters Dq and ζ are replaced by $-Dq$ and $-\zeta$, the $d^4(O_h^*)$ matrix will become a standard $d^6(O_h^*)$ matrix.

III. Changing of Energy Levels and States under Spin Transition

To describe the expansion of d orbitals of a transition metal ion caused by ligand field, we define a d orbital reduction factor N, which is similar to the covalency factor in the Curie formula.[28] The value N depends on the crystal field intensity and the covalency of the complex. Following the Curie formula,[28] the parameters B, C, and ζ in the matrix elements may be approximately expressed as

$$B = N^4B_0 \qquad C = N^4C_0 \qquad \zeta = N^2\zeta_0 \tag{17}$$

where B_0, C_0, and ζ_0 are the corresponding parameters of the ion in a free state and can be determined by its spectrum. For Fe(II), $B_0 = 3901$, $C_0 = 1058$, and $\zeta_0 = 410$ cm^{-1}. However, we will also adopt these values in the general studies for any d^6 ions. Then, for a given value of N, the electronic structure and the character in optics and magnetics of the system are entirely determined by the crystal field intensity Dq and independent of the details of the ligands. In our calculations we will take a typical value of N and a set of values of Dq to calculate the eigenvalues and eigenfunctions of the system for each Dq.

For a $d^6(O_h)$ ion with out S−O coupling, it can be seen from the Sugano diagram obtained from the $d^6(O_h)$ matrix that in a

TABLE 1: Lowest Seven Eigenvalues (cm^{-1}) of a d^6(O_h^*) System[a]

$Dq-Dq_c$ (cm^{-1})								
32	−24	−16	−8	0	8	16	24	32
0 (T_2')	0 (T_2')	0 (T_2')	0 (T_2')	0 (T_2')	0 (A_1')	0 (A_1')	0 (A_1')	0 (A_1')
162 (E')	161 (E')	161 (E')	153 (A_1')	14 (A_1')	131 (T_2')	280 (T_2')	430 (T_2')	581 (T_2')
178 (T_1')	178 (T_1')	177 (T_1')	161 (E')	161 (E')	292 (E')	440 (E')	589 (E')	740 (E')
363 (A_1')	337 (A_1')	270 (A_1')	177 (T_1')	177 (T_1')	308 (T_1')	457 (T_1')	606 (T_1')	757 (T_1')
424 (T_1')	424 (T_1')	423 (T_1')	423 (T_1')	414 (A_1')	538 (A_1')	682 (A_1')	828 (A_1')	976 (A_1')
446 (T_2')	445 (T_2')	445 (T_2')	428 (A_1')	422 (T_1')	553 (T_1')	700 (T_1')	850 (T_1')	1000 (T_1')
677 (A_1')	550 (A_1')	464 (A_1')	444 (T_2')	444 (T_2')	574 (T_2')	723 (T_2')	872 (T_2')	1022 (T_2')

[a] Calculated with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $N = 0.95$, and $H = 0$. The value of Dq at the critical point is $Dq_c = 1373.95$ cm^{-1}. The symbol in parentheses following an eigenvalue is the O_h^* irreducible representation that the corresponding eigenstates belong to. The degeneracy of an eigenvalue that belongs to A_1', E', T_1', and T_2' are respectively 1, 2, 3, and 3.

wide region of Dq the lowest two states will be $^1A_1$ and $^5T_2$. The energy difference is, if neglecting the configuration interactions,

$$\delta = E(^1A_1) - E(^5T_2) = 8C + 5B - 20Dq \qquad (18)$$

Which state is the ground one is determined by the sign of δ, i.e., determined by the competition of the crystal field energy (20Dq) and the electrostatic energy (8C + 5B). When the crystal field energy reaches a balance with the electrostatic energy, i.e., when $\delta = 0$, the two states will intersect with each other, thus leading to spin transition. Therefore the critical crystal field intensity Dq_c is determined by the transition condition

$$20Dq = 8C + 5B \qquad (19)$$

Using the approximation formula (17), Dq_c will be entirely determined by N through the following formula:

$$20Dq_c = (8C_0 + 5B_0)N^4 \qquad (20)$$

However, in a real d^6(O_h^*) system the S−O coupling will break each $S\Gamma$ term into several substates and causes a term mixture. Each eigenfunction will be a linear combination of substates with different spins and different symmetries and thus there is no pure $^1A_1$ or $^5T_2$ state. Therefore the real spin transition course can only be sought in the substates of $^1A_1$ and $^5T_2$ and the transition point will be changed.

When the system is certainly in HS or LS state, the symbol $\Gamma'(S\Gamma)$, e.g., $A'(^5T_2)$, is customarily used to stand for a S−O splitting substate of the $S\Gamma$ term that belongs to the irreducible representation Γ' of O_h^*. So $S\Gamma$ is the mother term of $\Gamma'(S\Gamma)$ and also its main multiplet component. However, if the system is in a course of spin transition, the multiplet components in an eigenstate will be, in general, gradually changed and cannot be certain and thus need a dynamic description. Now, to give a detailed description of the spin transition course, we introduce a dynamic notation $\Gamma'_{,k}(S_1\Gamma_1{-}S_2\Gamma_2)$, e.g., $A'_{1,1}(^5T_2{-}^1A_1)$, to stand for the kth eigenvalue as well as the corresponding set of eigenstates of the $\Gamma'\gamma'$ block according to ascending order. Such a notation represents an eigenstate changing from a quasi-$S_1\Gamma_1(O_h)$ state into a quasi-$S_2\Gamma_2(O_h)$ state when Dq increases to lead to a HS → LS spin transition. That is, its mother term is $S_1\Gamma_1(O_h)$ when Dq is small but $S_2\Gamma_2(O_h)$ when Dq is large.

In Table 1 we list the lowest seven eigenvalues (corresponding to 16 eigenstates) for each $Dq-Dq_c$; the corresponding energy curves are given in Figure 1. The changes in the multiplet fraction in the lowest 25 eigenstates (corresponding to 11 eigenvalues) are shown in Table 2. The changes in the HS fraction of the most important three sets of eigenstates are shown in Figure 2.

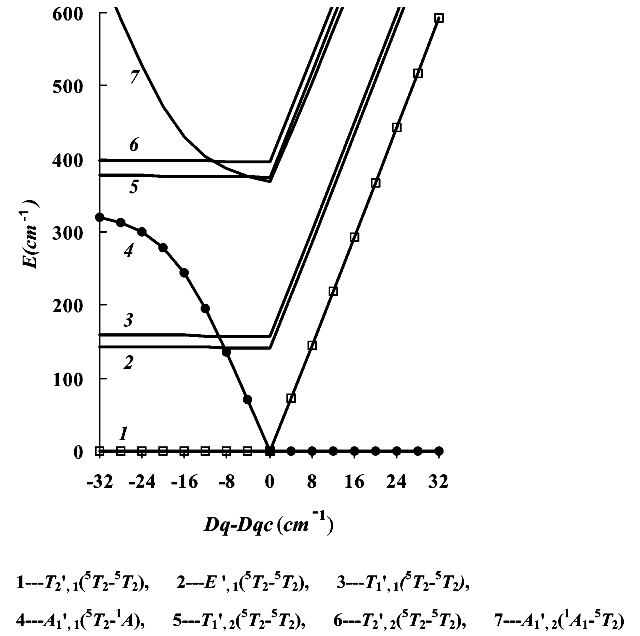

Figure 1. Lowest seven energy levels of a d^6(O_h^*) system near the spin-transition critical point. Calculated with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $N = 0.95$, and $H = 0$, leading to $Dq_c = 1373.95$ cm^{-1}.

It can be seen from Figure 1 and Table 2 that for the HS → LS spin transition the lowest substate $A'_{1,2}(^1A_1{-}^5T_2)$ of $^1A_1$ transfers its $^1A_1$ component to the substate $A'_{1,1}(^5T_2{-}^1A_1)$ of $^5T_2$, and the latter crosses the lowest substate $T'_{2,1}(^5T_2{-}^5T_2)$ of $^5T_2$ at the critical point. They are the states that undertake direct responsibility for this spin transition. The spin-transition process will be described in detail in what follows.

From Table 2 we can see that, for small values of Dq, $A'_{1,1}(^5T_2{-}^1A_1)$ and $T'_{2,1}(^5T_2{-}^5T_2)$ are almost $^5T_2$, $A'_{1,2}(^1A_1{-}^5T_2)$ is almost $^1A_1$, $A'_{1,3}(^3T_1{-}^3T_1)$ is almost $^3T_1$. With increasing Dq, a change of multiplet fraction occurs in and only in $A'_{1,1}(^5T_2{-}^1A_1)$ and $A'_{1,2}(^1A_1{-}^5T_2)$. At any moment the decrease of the HS fraction in $A'_{1,1}(^5T_2{-}^1A_1)$ is equal to the increase of that in $A'_{1,2}(^1A_1{-}^5T_2)$ (see also Figure 2), the increase of the LS fraction in $A'_{1,1}(^5T_2{-}^1A_1)$ is equal to the decrease of that in $A'_{1,2}(^1A_1{-}^5T_2)$. That is, multiplet components exchange between $A'_{1,1}(^5T_2{-}^1A_1)$ and $A'_{1,2}(^1A_1{-}^5T_2)$. This is because a S−O coupling can occur between each of them and the quasi-$^3T_1$ state $A'_{1,3}(^3T_1{-}^3T_1)$, although this coupling cannot occur directly between them. Such an exchange changes $A'_{1,1}(^5T_2{-}^1A_1)$ from a quasi-$^5T_2$ gradually into a quasi-$^1A_1$ state, and $A'_{1,2}(^1A_1{-}^5T_2)$ from a quasi-$^1A_1$ into a quasi-$^5T_2$ state. At the same time, the energy curve of $A'_{1,2}(^1A_1{-}^5T_2)$ descends gradually to $A'_{1,1}(^5T_2{-}^1A_1)$ and then begins to ascend, but $A'_{1,1}(^5T_2{-}^1A_1)$ descends continuously owing to the

TABLE 2: Fractions of the Main Multiplets in the Lowest 25 Eigenstates of a $d^6(O_h^*)$ System[a]

		$Dq - Dq_C$ (cm^{-1})								
state	multiplet	−32	−24	−16	−8	0	8	16	24	32
$A'_{1,1}(^5T_2{-}^1A_1)$	$^5T_2$	.8840	.7191	.3572	.1267	.0540	.0283	.0169	.0111	.0078
	$^1A_1$	.0915	.2493	.6056	.8389	.9150	.9432	.9563	.9635	.9680
$A'_{1,2}(^1A_1{-}^5T_2)$	$^5T_2$	.1030	.2676	.6291	.8593	.9316	.9570	.9679	.9733	.9762
	$^1A_1$	.8824	.7253	.3698	.1371	.0616	.0341	.0216	.0150	.0111
$A'_{1,3}(^3T_1{-}^3T_1)$	$^3T_1$	.9620	.9625	.9628	.9631	.9634	.9637	.9638	.9640	.9641
$T'_{2,1}(^5T_2{-}^5T_2)$	$^5T_2$	.9985	.9984	.9984	.9984	.9984	.9984	.9984	.9983	.9983
$T'_{2,2}(^5T_2{-}^5T_2)$	$^5T_2$	.9934	.9932	.9930	.9928	.9926	.9923	.9921	.9918	.9915
$T'_{2,3}(^3T_1{-}^3T_1)$	$^3T_1$	.9920	.9918	.9916	.9914	.9911	.9909	.9906	.9903	.9901
$E'_{,1}(^5T_2{-}^5T_2)$	$^5T_2$	.9942	.9940	.9939	.9938	.9936	.9935	.9933	.9931	.9930
$E'_{,2}(^3T_1{-}^3T_1)$	$^3T_1$	.9921	.9920	.9919	.9917	.9916	.9915	.9914	.9913	.9911
$T'_{1,1}(^5T_2{-}^5T_2)$	$^5T_2$	.9965	.9964	.9964	.9963	.9962	.9961	.9960	.9959	.9958
$T'_{1,2}(^5T_2{-}^5T_2)$	$^5T_2$	.9910	.9908	.9905	.9903	.9900	.9897	.9894	.9891	.9888
$T'_{1,3}(^3T_1{-}^3T_1)$	$^3T_1$	.9883	.9880	.9877	.9874	.9871	.9867	.9864	.9860	.9856

[a] Calculated with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $N = 0.95$, and $H = 0$. The critical Dq is $Dq_c = 1373.95$ cm^{-1}. A rapid change in multiplet fraction can be seen only in the eigenstates $f_1(A'_1)$ and $f_2(A'_1)$. The multiplet components in other eigenstates remain almost unchanged.

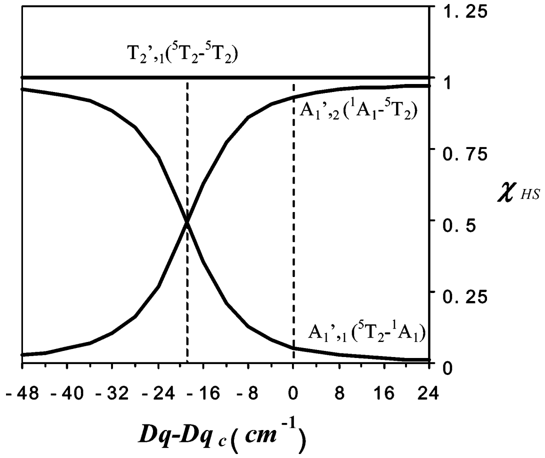

Figure 2. HS fraction χ_{HS} in the most important three sets of eigenstates of an octahedrally coordinated d^6 ion. Calculated with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $N = 0.95$, and $H = 0$, leading to $Dq_c = 1373.95$ cm^{-1}. The HS fractions of $A'_{1,1}(^5T_2{-}^1A_1)$ and $A'_{1,2}(^1A_1{-}^5T_2)$ become equal when $Dq{-}Dq_c \simeq -18.75$ (cm^{-1}).

increase in its $^1A_1$ fraction; thus they do not intersect. When Dq reaches a threshold point, the continuously descending $A'_{1,1}(^5T_2{-}^1A_1)$, in which the $^1A_1$ fraction already dominated, intersects with $T'_{2,1}(^5T_2{-}^5T_2)$ and becomes the ground state, thus leading to an HS → LS spin transition. Such a threshold point is the spin-transition point, and such a Dq value is called the critical crystal field intensity, denoted by Dq_c. Thus it can be seen that the HS → LS spin transition is an intersection between two substates of $^5T_2$ instead of an intersection between $^1A_1$ and $^5T_2$. Figure 2 shows the curves of the HS fraction of $A'_{1,1}(^5T_2{-}^1A_1)$, $A'_{1,2}(^1A_1{-}^5T_2)$, and $T'_{2,1}(^5T_2{-}^5T_2)$ vs $Dq{-}Dq_c$.

Let us examine the multiplet fraction in the ground state. In our opinion, around the critical point, the ground state is the approximately degenerate state formed by the lowest eigenstates $A'_{1,1}(^5T_2{-}^1A_1)$ and $T'_{2,1}(^5T_2{-}^5T_2)$, they are close to each other and far from the upper levels. The degeneracy of $A'_{1,1}(^5T_2{-}^1A_1)$ and $T'_{2,1}(^5T_2{-}^5T_2)$ are 1 and 3, respectively, their HS fractiona at the critical point are 0.054 and 0.9984 (see Table 2 and Figure 2), respectively; thus the HS fraction in the ground state is $\chi_{HS} = (0.054 + 3 \times 0.9984)/4 = 0.7623$ instead of the arithmetic average value 0.5. This is to say, the point at which $\chi_{HS} = 0.5$ is not the spin-transition point. The change of HS and LS fractions in the ground state are shown respectively by the curves χ_{HS} and χ_{LS} in Figure 3. The HS fraction in the lowest eigenstate, as described by curve b, changes abruptly at the critical point from 0.054 to 0.9984.

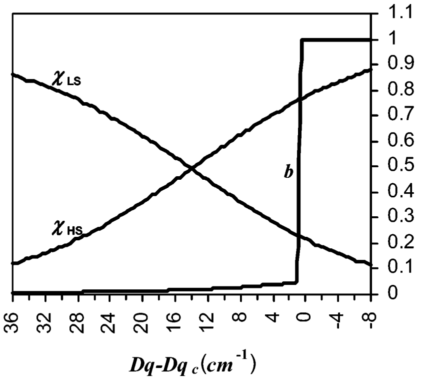

Figure 3. HS and LS fractions in the ground state of a $d^6(O_h^*)$ ion. Calculated near the spin-transition critical point, with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $N = 0.95$, and $H = 0$, leading to $Dq_c = 1373.95$ cm^{-1}. The direction of the abscissa is opposite to that in Figures 1 and 2.

Finally we give an approximate formula for calculating the real critical crystal field intensity Dq_c of an octahedrally coordinated Fe(II) as follows

$$Dq_c = -17.9N + 1703.3585N^{3.95} \tag{21}$$

For $N = 0.95$, we have now $Dq_c = 1373.95$ cm^{-1}. An increase in N means a decrease in the d orbital expansion, leading to an increase in Dq_c. If the relation between Dq and temperature T is known, one can determine the spin transition temperature T_c by Dq_c and thus by N. Considering that, besides temperature, other perturbations may also change Dq and lead to spin transition, we prefer to take Dq rather than T as the argument in a general study of spin transition.

IV. Molecular Magnetic Behavior in Spin Transition

The molecular magnetic properties of HS and LS states are essentially different, and in a HS ⇄ LS spin transition it will change from one case into another. The molecular effective moment μ_{eff} can be calculated by the Van Vleck formula:[27]

$$\mu_{eff}^{\ 2} = 3kT\frac{\sum_i [(W_i^{(1)})^2/kT - 2W_i^{(2)}]e^{-W_i^{(0)}/kT}}{\sum_i e^{-W_i^{(0)}/kT}} \tag{22}$$

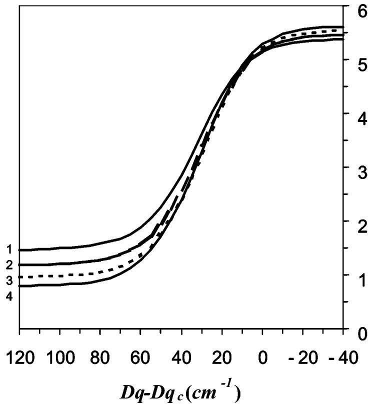

Figure 4. $\mu_{\text{eff}}-Dq$ cures of a d^6 ion at $T = 300$ K. Curves 1−4 correspond to $N = 0.7$, 0.8, 0.9, 1.0, respectively. For all curves, $\mu_{\text{eff}} \approx 5.2$ at the spin-transition point, the saturation $\mu_{\text{eff}} \approx 5.5$ and the low spin μ_{eff} is greater than zero remarkably.

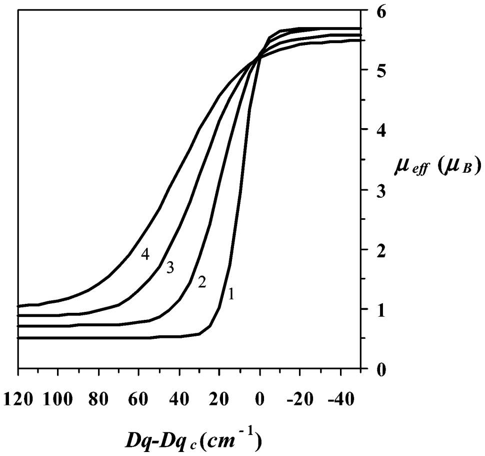

Figure 5. $\mu_{\text{eff}}-Dq$ curves of a d^6(O_h^*) ion with $N = 0.95$. Curves 1−4 correspond to $T = 100$, 200, 300, 400 K, respectively. For all curves, $\mu_{\text{eff}} \approx 5.2$ at the spin-transition point, the saturation $\mu_{\text{eff}} \approx 5.5$, and the low-spin μ_{eff} is greater than zero remarkably.

where $W_i^{(0)}$, $W_i^{(1)}$ and $W_i^{(2)}$ are the first three coefficients in the following expanded form of the eigenvalues of the complete energy matrix in terms of $H' = \beta H$, where H is the weak magnetic field and β is the Bohr magneton.

$$E_i = W_i^{(0)} + H'W_i^{(1)} + H'^2W_i^{(2)} \ldots \qquad (i = 1-210) \qquad (23)$$

Giving three values for H', we can obtain three such expanded forms, and if we cut off the terms higher than H'^2, we can calculate the W coefficients from the three equations. It is known from the Van Vleck theorem[27] that the calculation of μ_{eff} may be carried out in a cubic field approximation if the matrix elements of the low-symmetry field are all smaller than kT (at room temperature $kT \approx 200$ cm^{-1}).

In what follows we will discuss the changing rule of μ_{eff} in the spin transition based on the calculation results with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $B = N^4B_0$, $C = N^4C_0$, and $\zeta = N^2\zeta_0$.

1. $\mu_{\text{eff}}-Dq$ Curves for Different N and Fixed T. In Figure 4 a set of curves of μ_{eff} vs Dq has been given for $N = 0.7$, 0.8, 0.9, 1.0 and fixed $T = 300$ K. All curves intersect approximately at one point, which is the spin-transition critical point and corresponds to $\mu_{\text{eff}} \approx 5.22\mu_B$, near the saturated value $5.5\mu_B$.

2. $\mu_{\text{eff}}-Dq$ Curves for Different T and Fixed N. In Figure 5 a set of curves of μ_{eff} vs Dq has been given for $T = 100$, 200, 300, 400 K and fixed $N = 0.95$. All curves intersect approximately at one point, which is the spin-transition critical point and corresponds to $\mu_{\text{eff}} \approx 5.22\mu_B$, near the saturated value $5.5\mu_B$.

3. $\mu_{\text{eff}}-T$ Curve. In above two sections we have obtained a group of theoretical $\mu_{\text{eff}}-Dq$ curves. To obtain the $\mu_{\text{eff}}-T$ relation, we must obtain the T dependence of Dq. It is well-known that Dq is generally expressed as

$$Dq = \frac{-eq_0\langle r^4\rangle}{6R^5}$$

with

$$\langle r^k\rangle = \int_0^R R_d^{\,2}(r)r^kr^2\,\mathrm{d}r + R^{2k+1}\int_R^\infty R_d^{\,2}(r)r^{-k-1}r^2\,\mathrm{d}r$$

where e is the charge of an electron, q_0 is the effective charge of a ligand, $R_d(r)$ is the radial wave function of the d electrons, r is radial coordinates, and R is bond length. It is obvious that Dq is a function of R. Because R depends on T, Dq depends on T. An increase in T leads to an increase in R by pure thermal expansion; this increase in R leads to a decrease in Dq according to the above formula. This is only one side of the problem. The other side, the most important, is, in the neighborhood of the spin-transition critical point, the above decrease in Dq leads to a rapid increase in the HS fraction of the ground state that leads to a rapid increase in R, from the smaller LS bond length toward the larger HS bond length; this increase in R again leads to a further decrease in Dq. This is a positive feedback effect, as graphically shown below,

$$\text{(LS state)} \qquad T\uparrow \Rightarrow R\uparrow \Rightarrow Dq\downarrow \Rightarrow R\uparrow \Rightarrow Dq\downarrow \Rightarrow \cdots \Rightarrow \text{(HS state)}$$

It is this positive feedback effect that leads to the spin transition from the LS into the HS state. The T dependence of Dq is so complicated that it is impossible to obtain by a pure theoretical method. In what follows we will seek it by a method of combining theory with experiments.

The calculation results in paragraph 1 and 2 of section IV show an important feature of the octahedrally coordinated d^6 ions that the effective molecular magnetic moment at the spin-transition point is $\mu_{\text{eff}} \approx 5.22\mu_B$. On the other hand, this value in the experimental $\mu_{\text{eff}}-T$ curve[1] for the Fe(II) ion corresponds to $T = 270$ K. That is to say, the spin-transition temperature of the Fe(II) ions is $T_c \approx 270$ K. Again, we found that the shape of our theoretical $\mu_{\text{eff}}-Dq$ curves (see Figures 4 and 5) are similar to the experimental $\mu_{\text{eff}}-T$ curve.[1] If the theoretical $\mu_{\text{eff}}-Dq$ curves correspond to a function relation

$$\mu_{\text{eff}} = f(Dq)$$

and the experimental $\mu_{\text{eff}}-T$ curve corresponds to

$$\mu_{\text{eff}} = \varphi(T)$$

and if the two kinds of curves are strictly similar, then we have

$$\varphi(x) = f(ax + b)$$

Thus we have

$$\mu_{\text{eff}} = f(Dq)$$

$$\mu_{\text{eff}} = f(aT + b)$$

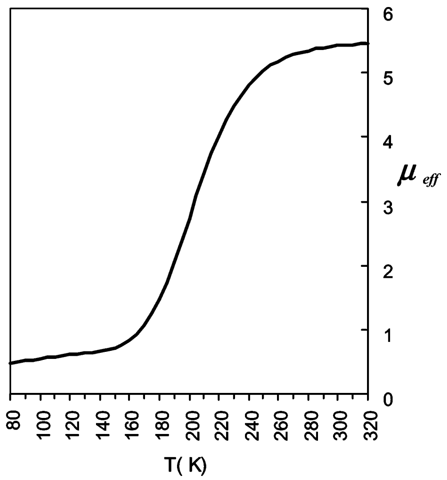

Figure 6. Theoretical $\mu_{\rm eff}-T$ curve for an octahedrally coordinated Fe(II) ion. At $T = 90$, 270, and 293 K the experimental $\mu_{\rm eff}$ values[1] are respectively 0.76, 5.22, and $5.4\mu_{\rm B}$; the theoretical $\mu_{\rm eff}$ values are respectively 0.51, 5.28, and $5.4\mu_{\rm B}$. Calculated with $B_0 = 3901$, $C_0 = 1058$, $\zeta_0 = 410$ cm^{-1}, $B = N^4B_0$, $C = N^4C_0$, $\zeta = N^2\zeta_0$, and $N = 0.95$.

This leads to a linear relationship

$$Dq = aT + b$$

where a and b are constants. Because the similarity of the two kinds of curves is not strict, the T dependence of Dq should be approximately linear. From this we introduce a second-order term and suppose $Dq-T$ relation as

$$Dq = a_0 - a_1T + a_2T^2 \tag{24}$$

where a_0, a_1, and a_2 are constants and can be determined by three set of data from the $\mu_{\rm eff}-T$ experiment[1], i.e., $\mu_{\rm eff}(90{\rm K}) = 0.76\mu_{\rm B}$, $\mu_{\rm eff}(270{\rm K}) = 5.22\mu_{\rm B}$, and $\mu_{\rm eff}(293{\rm K}) = 5.4\mu_{\rm B}$. By fitting these experimental points, we obtained

$$a_0 = 1510.7 \qquad a_1 = 0.6929 \qquad a_2 = 0.00069$$

These constants show that the second-order term in (24) is indeed very small. Substituting (24) for the Dq in the complete $d^6(O_h^*)$ matrix, we obtained a theoretical $\mu_{\rm eff}-T$ curve (Figure 6) and especially $\mu_{\rm eff}(90{\rm K}) = 0.51\mu_{\rm B}$, $\mu_{\rm eff}(293{\rm K}) = 5.4\mu_{\rm B}$, and $\mu_{\rm eff}(270{\rm K}) = 5.28\mu_{\rm B}$. The functional form of (24) comes from ascending experiments for octahedrally coordinated d^6 systems in the spin-transition region. Of course, its general validity should be checked by further experiments.

The theoretical results in all the above subsections 1−3 show that for any octahedrally coordinated d^6 ion at the HS ↔ LS spin-transition point the $\mu_{\rm eff}$ value is approximately $5.22\mu_{\rm B}$ instead of the arithmetic average of the two values in the HS and LS states, as is usually expected. This is mainly because the LS and HS states, which are included in the ground state and intersect each other at the critical point, have degeneracies of 1 and 3, respectively, and thus have different statistical weights, and besides, all high levels can contribute to $\mu_{\rm eff}$.

V. Conclusions

We have the following conclusions for any octahedrally coordinated d^6 ion.

(1) In the HS → LS spin transition, with Dq increasing from a small value, the lowest substate $A'_{1,2}(^1A_1{-}^5T_2)$ of $^1A_1$ transfers continually its $^1A_1$ components to the substate $A'_{1,1}(^5T_2{-}^1A_1)$ of $^5T_2$, changing the latter continually from a quasi-$^5T_2$ into a quasi-$^1A_1$ state, and the latter intersects with the lowest substate $T'_{2,1}(^5T_2{-}^5T_2)$ of $^5T_2$ at a certain point. That is, the spin transition is an intersection between two substates of $^5T_2$. This is by no means a simple spin transition between $^5T_2$ and $^1A_1$.

(2) The Dq value at the spin-transition point is determined by the intensity of the electrostatic interaction between the d-electrons and influenced by S−O coupling. In our method, it is determined by the value of the d orbital reduction factor N. For Fe(II) ions we have $Dq_{\rm c} = -17.9N + 1703.3585N^{3.95}$.

(3) Around the spin-transition critical point, the ground state is the approximately degenerate state formed by the lowest four eigenstates, i.e., the nondegenerate $A'_{1,1}(^5T_2{-}^1A_1)$ and the 3-fold degenerate $T'_{2,1}(^5T_2{-}^5T_2)$.

(4) At the HS ↔ LS spin-transition point, the $\mu_{\rm eff}$ value is approximately $5.22\mu_{\rm B}$ instead of the arithmetic average of the values in the HS and LS states as is usually expected.

(5) In either the HS or LS state the value of $\mu_{\rm eff}$ is evidently larger than that calculated by the Curie formula $\mu_{\rm eff}^2 = \mu_{\rm B}^2 g_{\rm s}^2 S(S + 1)$ and in agreement respectively with the experimental values $5.4\mu_{\rm B}$ and $0.76\mu_{\rm B}$ of the Fe(II) ion.[1] This is because the orbital magnetic moments have not been completely annihilated by the crystal field and thus can contribute to $\mu_{\rm eff}$. This is true for any octahedrally coordinated d^6 ions and need not be explained by an influence from Fe(III) impurity as Lemercier et al. supposed.[1]

(6) The $Dq-T$ relation in the spin-transition region is approximately linear. As for the Fe(II) ions, our theoretical values of $\mu_{\rm eff}$ and the $\mu_{\rm eff}-T$ curve agree well with Lemercier et al.'s experimental findings.[1]

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