Ligand Field-Spin Orbit Energy Levels in the d^4 and d^6 Electron Configurations of Octahedral and Tetrahedral Symmetry

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The complete ligand field–Coulomb repulsion–spin orbit interaction matrices have been derived for the d^4 and d^6 electron configurations within octahedral (O_h) and tetrahedral (T_d) symmetry. The calculations were performed in both the weak-field and strong-field coupling schemes and complete agreement of the results was achieved. The energy matrices are parametrically dependent on ligand field (Dq), Coulomb repulsion (B, C) and spin-orbit interaction (ζ). Correct energy diagrams are presentend which display the splittings by spin-orbit perturbation as well as the effect of configuration mixing. Applications to the interpretation of optical spectral data, to the detailed behavior at the crossover of ground terms, and to complete studies in magnetism are pointed out.

1. Introduction

Calculations involving the combined effect of the ligand field and spin-orbit interactions ("complete ligand field theory") have been reported, in octahedral and tetrahedral symmetry, for the d^2, d^8 and d^3, d^7 electronic configurations[1,2]. These results contributed in the past to a better understanding of the electronic structure of corresponding transition metal complexes. The more complicated problems within the d^n series, *viz.* d^4, d^6 and d^5 having a total degeneracy of 210 and 252, respectively, have received only little attention so far. In the d^4 configuration, in particular, matrix elements in both the strong-field[3] and the weak-field[4] coupling scheme have been reported. However, detailed numerical calculations have not been attempted and, therefore, the correctness of these algebraic results has not been established beyond doubt. Indeed, numerous errors have been detected recently in the above mentioned weak-field matrix elements[5,6]. The few attempts that have been advanced at the interpretation of electronic spectra[7] employed energy levels without spin-orbit coupling and with partial neglect of configuration interaction. We have shown recently[8] that, in the complementary configuration d^6, configuration interaction with relatively high energy levels may seriously affect even the electronic ground state of certain systems. It is evident that the correct inclusion of configuration interaction becomes indispensable in any attempt at an assignment of spectral transition energies. On the other hand, spin-orbit interaction produces only minor splittings and energy shifts within the 3d transition series, while it is a major energy contribution in systems involving 4d and 5d transition metal ions.

The purpose of the present investigation is to rederive the complete energy levels of the d^4 and d^6 electron configurations in ligand fields of octahedral and tetrahedral symmetries including spin-orbit as well as complete configuration interaction. The derivation will be effected in both the weak-field and the strong-field coupling schemes. The correctness of the results should then be established by extended cross-checks of detailed numerical data computed within both schemes. In addition, employment of the available matrix elements[3,4] should demonstrate their correctness or otherwise. Applications of the results to the interpretation of optical spectra and other experimental data will be reserved to a forthcoming paper.

2. Theoretical Basis

The appropriate Hamiltonian considered in the present study consists of the cubic ligand field potential, the electron-electron repulsion, and the spin-orbit interaction operators

$$\mathcal{H} = V_{\mathrm{LF}}(r, \theta, \varphi) + \sum_{i>j}^{4} \frac{e^2}{r_{ij}} + \sum_{i}^{4} \xi(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i \,. \qquad (1)$$

A single electron within a ligand field of octahedral symmetry is subject to a potential having the explicit form

$$V_{O_h} = \tfrac{7}{2}\{C_0^{(4)}(\theta, \varphi) + (\tfrac{5}{14})^{1/2} \times [C_4^{(4)}(\theta, \varphi) + C_{-4}^{(4)}(\theta, \varphi)]\} \frac{Z e^2}{a^5} r^4 \qquad (2)$$

where the rationalized form of spherical harmonics introduced by Racah [9] has been employed. The relation between the $C_q^{(k)}$ and the well-known Y_{kq} is

$$C_q^{(k)} = \left[\frac{4\pi}{(2k+1)}\right]^{1/2} Y_{kq} . \tag{3}$$

In the calculations to be described below two different coupling schemes will be utilized. In the weak-field coupling, the sequence according to which the perturbations of Eq. (1) are applied is

$$\sum_{i>j} e^2/r_{ij} > \sum_i \xi(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i > V_{\mathrm{LF}}(r, \theta, \varphi) \tag{4}$$

whereas in the strong-field coupling the sequence is as follows

$$V_{\mathrm{LF}}(r, \theta, \varphi) > \sum_{i>j} e^2/r_{ij} > \sum_i \xi(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i . \tag{5}$$

Provided all state functions of the configuration in question have been properly included, both coupling schemes produce identical eigenvalues of the energy. However, the methods differ by the characterization of the resulting energy levels.

3. Weak-Field Coupling

Wave Functions. In the four- and the six-electron problem, the usual procedure [10] of setting-up symmetry adapted cubic wave functions in coordinate space is cumbersome if not difficult. Therefore, vector coupling techniques have been prefered. The ket vectors $|v\,L\,M_{\mathrm{L}}\rangle$ transforming according to the irreducible representation D^{L} of the group R_3 which are appropriate to the first term of Eq. (4) are formed from the one-electron functions $|n\,l\,m_l\rangle$ taking two functions at one time. It is thus

$$|l_1\, l_2\, L_{12}\, M_{\mathrm{L}12}\rangle = \sum_{m_{l1},\, m_{l2}} \cdot |l_1\, m_{l1}\rangle |l_2\, m_{l2}\rangle \times \langle l_1\, m_{l1}\, l_2\, m_{l2} | L_{12}\, M_{L12}\rangle . \tag{6}$$

States having the same value of L are being distinguished by the seniority number v. Since $\Sigma e^2/r_{ij}$ is independent of spin, the antisymmetric many electron wave functions in R_3 are simply the product of coupled orbital functions with coupled spin functions

$$|v\,S\,M_{\mathrm{S}}\,L\,M_{\mathrm{L}}\rangle = |S\,M_{\mathrm{S}}\rangle |v\,L\,M_{\mathrm{L}}\rangle . \tag{7}$$

Functions corresponding to the joint effect of the first and second term of Eq. (4) transform according to $D^{\mathrm{S}} \times D^{\mathrm{L}} = \Sigma D^{\mathrm{J}}$ and, therefore, these are determined by

$$|v\,S\,L\,J\,M_{\mathrm{J}}\rangle = \sum_{M_{\mathrm{S}},\, M_{\mathrm{L}}} |v\,S\,M_{\mathrm{S}}\,L\,M_{\mathrm{L}}\rangle \langle S\,M_{\mathrm{S}}\,L\,M_{\mathrm{L}} | J\,M_{\mathrm{J}}\rangle . \tag{8}$$

Finally, the wave functions of the combined operator of Eq. (4) transform according to irreducible representations Γ_i of the molecular point group where $D^{\mathrm{J}} = \Sigma a_i \Gamma_i$. These functions are given as follows

$$|\alpha\, J\, \Gamma\, \gamma\, a\rangle = \sum_{M_J} |\alpha\, J\, M_{\mathrm{J}}\rangle \langle J\, M_{\mathrm{J}} | \Gamma\, \gamma\, a\rangle \tag{9}$$

where the expansion coefficients $\langle J\, M_{\mathrm{J}} | \Gamma\, \gamma\, a\rangle$ may be determined, *e. g.* by the projection operator technique [11]. In Eq. (9), α stands for any additional quantum numbers required, γ denotes a specific row in the irreducible representation Γ and a is needed to distinguish a particular function from among several of the same kind if Γ occurs more than once in the reduction $D^{\mathrm{J}} \rightarrow \Sigma a_i \Gamma_i$.

Matrix Elements. The Coulomb electron-electron repulsion operator for four electrons is of type $\boldsymbol{G}$, *i. e.* it is the sum of two-electron operators $\boldsymbol{g}_{ij}$

$$\boldsymbol{G} = \sum_{i>j}^{4} \boldsymbol{g}_{ij} = \sum_{i>j}^{4} e^2/\boldsymbol{r}_{ij} . \tag{10}$$

Consequently, the matrix elements $\langle u | \boldsymbol{G} | v\rangle$ between the two states u and v vanish if the states differ in the coordinates of more than two electrons. The calculation may be based on the use of two-particle coefficients of fractional parentage [12]. An alternate approach distinguishes the three cases where u and v are either identical or differ by one or two single-electron functions [13]. In the simple case of equivalent electrons, the individual matrix elements are of the form

$$\langle (n\,l)^2\, S\, L | e^2/\boldsymbol{r}_{12} | (n\,l)^2\, S\, L\rangle = \sum_k (-1)^L \langle l \| \boldsymbol{C}^{(k)} \| l\rangle \begin{Bmatrix} l & l & k \\ l & l & L \end{Bmatrix} F^k(n\,l, n\,l) . \tag{11}$$

Here, $\langle l \| C^{(k)} \| l\rangle$ is a reduced matrix element of the irreducible tensorial operator corresponding to the spherical harmonics of Eq. (3), the quantity in braces is a 6-j coefficient [14], and the radial integrals $F^k(n\,l, n\,l)$ may be redefined [13], for d electrons, in terms of the Slater-Condon parameters F_0, F_2, and F_4 or in terms of the Racah parameters $A = F_0 - 49\,F_4$, $B = F_2 - 5\,F_4$, and $C = 35\,F_4$. The latter set of parameters will be adopted in the present study.

The matrix elements of spin-orbit interaction may be written

$$\begin{aligned}&\langle \alpha S L J M | \sum_i \xi(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i | \alpha' S' L' J M \rangle \\ &= \zeta_{nl} (-1)^{J+L+S'} [l(l+1)[l]]^{1/2} \begin{Bmatrix} L & L' & 1 \\ S' & S & J \end{Bmatrix} \\ &\times \langle \alpha S L \| \mathbf{V}^{(11)} \| \alpha' S' L' \rangle\end{aligned} \tag{12}$$

where we have introduced the usual abbreviation for dimension, *i. e.* $[j] = 2j+1$, and where ζ_{nl} is the spin-orbit coupling parameter. The reduced matrix element of the double tensor $\mathbf{V}^{(11)}$ may be expressed according to

$$\begin{aligned}&\langle \alpha S L \| \mathbf{V}^{(11)} \| \alpha' S' L' \rangle \\ &= (-1)^{S+L+s+l} N [s(s+1)[s][S][L][S'][L']]^{1/2} \\ &\times \sum_{\bar{\alpha}, \bar{S}, \bar{L}} (-1)^{\bar{S}+\bar{L}} \begin{Bmatrix} S & S' & 1 \\ s & s & \bar{S} \end{Bmatrix} \begin{Bmatrix} L & L' & 1 \\ l & l & \bar{L} \end{Bmatrix} \\ &\times \langle \alpha S L \{ | \bar{\alpha} \bar{S} \bar{L} \rangle \langle \bar{\alpha} \bar{S} \bar{L} | \} \alpha' S' L' \rangle .\end{aligned} \tag{13}$$

In Eq. (13), N is the number of d electrons in d^N, the quantities $\langle \bar{\alpha} \bar{S} \bar{L} | \} \alpha S L \rangle$ are known as coefficients of fractional parentage[12], and the barred states $\bar{\alpha} \bar{S} \bar{L}$ of l^{N-1} are the parents of the state $\alpha S L$ of l^N.

Since we may expand the single-electron ligand field potential in terms of the tensor operators $\boldsymbol{C}_q^{(k)}$ [15, 16]

$$V_{\mathrm{LF}} = \sum_{k,q} B_q^k \boldsymbol{C}_q^{(k)} \tag{14}$$

the following general expression for the matrix elements of V_{LF} may be obtained

$$\begin{aligned}&\langle \alpha S L J \Gamma \gamma a | V_{\mathrm{LF}} | \alpha' S' L' J' \Gamma' \gamma' a' \rangle \\ &= \delta(\Gamma, \Gamma') \delta(\gamma, \gamma') \sum_{k,q} B_q^k \sum_{M, M'} \langle \Gamma \gamma a | J M \rangle \\ &\times \langle \alpha S L J M | \sum_i^N \boldsymbol{C}_q^{(k)}(i) | \alpha' S' L' J' M' \rangle \\ &\times \langle J' M' | \Gamma \gamma a' \rangle .\end{aligned} \tag{15}$$

The matrix element of the tensor operator $\boldsymbol{C}_q^{(k)}$ of rank k may be obtained according to

$$\begin{aligned}&\langle \alpha S L J M | \sum_i^N \boldsymbol{C}_q^{(k)}(i) | \alpha' S' L' J' M' \rangle \\ &= \delta(S, S') (-1)^{S+L+L'+J-k-l} \langle J' M' k q | J M \rangle \\ &\times \langle l 0 k 0 | l 0 \rangle \{[L][L'][J][l]\}^{1/2} \\ &\times N \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix} \sum_{\bar{\alpha}, \bar{L}} (-1)^{\bar{L}} \langle \alpha S L \{ | \bar{\alpha} \bar{S} \bar{L} \rangle \\ &\times \langle \bar{\alpha} \bar{S} \bar{L} | \} \alpha' S' L' \rangle \begin{Bmatrix} L & l & \bar{L} \\ l & L' & k \end{Bmatrix}\end{aligned} \tag{16}$$

where the various quantities have the same significance as discussed following Eq. (13) above.

The perturbation matrices for the combined Coulomb, spin-orbit, and ligand field interactions within the d^4 electron configuration subject to a field of O_h symmetry may then be calculated by a combination of the expressions in Eq. (11), Eq. (12), and Eq. (15). The blocked matrices characterized by the irreducible representations Γ_1, Γ_2, Γ_3, Γ_4, and Γ_5 are of dimension 14, 8, 19, 23 and 27, respectively. In contrast to the results of Dunn and Li [4–6], the matrix elements obtained by the present method are all real.

4. Strong-Field Coupling

Wave Functions. Here we start from the one-electron functions $|n l m_l\rangle$ transforming according to the irreducible representations D^l of R_3. On transition to a molecular point group $G \subset R_3$, these functions couple to yield the kets

$$|\Gamma_i \gamma_i\rangle = \sum_{m_l} |l m_l\rangle \langle l m_l | \Gamma_i \gamma_i \rangle . \tag{17}$$

The characterization in Eq. (17) uses the irreducible representation Γ_i and component γ_i according to the decomposition $D^l = \sum_i a_i \Gamma_i$. In cubic symmetry, this decomposition is into t_{2g} and e_g. Since the ligand field interaction is independent of spin, the spin orbitals may be written simply as

$$|s m_s \Gamma \gamma\rangle = |s m_s\rangle |\Gamma \gamma\rangle . \tag{18}$$

The required four-electron basis functions (*i. e.* the strong-field configurations) are then obtained as products of the one-electron functions Equation (17). The five different configurations are, in order of increasing energy: $[(t_{2g})^4]$, $[(t_{2g})^3(e_g)]$, $[(t_{2g})^2(e_g)^2]$, $[(t_{2g})(e_g)^3]$, and $[(e_g)^4]$. Functions corresponding to the combined effect of the first and second term in Eq. (5) transform as Γ_j in the decomposition

$$\Gamma_1 \times \Gamma_2 \times \Gamma_3 \times \Gamma_4 = \sum_j b_j \Gamma_j . \tag{19}$$

In the direct product of Eq. (19), Γ_1 to Γ_4 characterize the transformation of each of the four electrons. The resulting functions (terms) are then determined by step-wise coupling of two one-electron functions at one time, ultimately yielding

$$\begin{aligned}&|t_{2g}^m (S_1 \Gamma_1) e_g^n (S_2 \Gamma_2), S \Gamma M_S \gamma\rangle \\ &= \sum_{\substack{M_{S1}, M_{S2} \\ \gamma_1, \gamma_2}} |t_{2g}^m S_1 \Gamma_1 M_{S1} \gamma_1\rangle |e_g^n S_2 \Gamma_2 M_{S2} \gamma_2\rangle \\ &\times \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle \langle S_1 M_{S1} S_2 M_{S2} | S M_S \rangle .\end{aligned} \tag{20}$$

By this procedure, a correlation with weak-field functions is not required in order to determine the multiplicity. The terms arising from the octahedral d^4 system are as follows:

$$
\begin{aligned}
&t_{2g}^4: \quad {}^3T_1,\ {}^1A_1,\ {}^1E,\ {}^1T_2\\
&t_{2g}^3 e_g: {}^5E,\ {}^3A_1,\ {}^3A_2,\ 2\,{}^3E, 2\,{}^3T_1,\ 2\,{}^3T_2,\ {}^1A_1,\\
&\qquad {}^1A_2,\ {}^1E,\ 2\,{}^1T_1,\ 2\,{}^1T_2\\
&t_{2g}^2 e_g^2: {}^5T_2,\ {}^3A_2,\ {}^3E,\ 3\,{}^3T_1, 2\,{}^3T_2,\ 2\,{}^1A_1,\ {}^1A_2,\\
&\qquad 3\,{}^1E,\ {}^1T_1,\ 3\,{}^1T_2 \qquad (21)\\
&t_g^2 e_g^3: {}^3T_1,\ {}^3T_2,\ {}^1T_1,\ {}^1T_2\\
&e_g^4: \quad {}^1A_1
\end{aligned}
$$

All these terms are g according to parity. Finally, wave functions corresponding to the combined operator of Eq. (5) transform according to Γ_T where Γ_T results from the direct product of spin and orbital representations. *viz.* $\Gamma \times \Gamma_S = \Sigma\, c_T\, \Gamma_T$. The appropriate functions of these "total" states may be written as

$$
|\alpha S \Gamma \Gamma_T \gamma_T \beta\rangle = \sum_{M_S,\gamma} |\alpha S \Gamma M_S \gamma\rangle \langle S M_S \Gamma \gamma | \Gamma_T \gamma_T \beta\rangle\,. \qquad (22)
$$

In Eq. (22), β has been introduced to label repeated representations Γ_T having the same S and Γ.

Matrix Elements. The ligand field interaction energy within the set of functions $|\Gamma_i \gamma_i\rangle$ is easily calculated and, specifically, using the cubic basis $\{t_{2g}, e_g\}$ it is diagonal yielding the well-known result

$$
\begin{aligned}
\langle t_{2g} | V_{LF} | t_{2g}\rangle &= -4\,D\,q\,,\\
\langle e_g | V_{LF} | e_g\rangle &= \quad 6\,D\,q \qquad (23)
\end{aligned}
$$

where $10\,Dq = (5/3)\,(Z\,e^2/R^5)\,\langle r^4\rangle$. The ligand field energy of a strong-field configuration is then simply the algebraic sum of the energies Eq. (23) of the one-electron states composing the strong-field configuration in question.

The Coulomb electron-electron interaction energy may be treated in analogy to weak-field coupling. Thus matrix elements $\langle u | e^2/r_{ij} | v\rangle$ are zero unless u and v are either identical or unless u und v differ by one or two single-electron orbitals [13]. The non-vanishing matrix elements may then be calculated similar to Eq. (11) and are finally expressed in terms of the parameters F_0, F_2, and F_4 or, alternately, in terms of A, B, and C.

Matrix elements of spin-orbit interaction may be expressed on the basis of the generalized Wigner-Eckart theorem applied to the functions of Eq. (22), as

$$
\begin{aligned}
&\langle \alpha S \Gamma \Gamma_T \gamma_T \beta | \sum_i \xi(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i | \alpha' S' \Gamma' \Gamma_T' \gamma_T' \beta'\rangle\\
&\quad = \delta(\Gamma_T, \Gamma_T')\,\delta(\gamma_T, \gamma_T')\, c(S \Gamma S' \Gamma', \beta \Gamma_T) \qquad (24)\\
&\quad \times \langle \alpha S \Gamma \| \sum_i \xi(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i \| \alpha' S' \Gamma'\rangle\,.
\end{aligned}
$$

The coefficient $c(S \Gamma S' \Gamma', \beta \Gamma_T)$ which may be compared to the Racah coefficient in R_3 has been introduced by Griffith [17].

Some care has to be exercized if the coupling of spin and orbital functions produces functions transforming equally more than once. This situation occurs in octahedral symmetry only if $S > 1$ in conjunction with T_1 or T_2 orbital functions and the label β is then used to distinguish between these functions.

The perturbation matrices for the combined octahedral ligand field, Coulomb, and spin-orbit interactions in the electron configuration d^4 may then be set up by using the correct multiple of the expressions Eq. (23) in conjunction with Eq. (11) and Eq. (24). The blocked matrices characterized by the irreducible representations Γ_1, Γ_2, Γ_3, Γ_4, and Γ_5 are of the same dimensions as in weak-field coupling. Spin-orbit matrices for the octahedral d^4 problem have been derived previously by Schroeder [3]. To facilitate comparison of the two sets of results, the phases of wavefunctions Eq. (22) have been such chosen that the resulting matrix elements of spin-orbit interaction agree, as closely as possible, with those of Schroeder [3]. Nonetheless, four of the functions $|\alpha S \Gamma \Gamma_T \gamma_T \beta\rangle$ generated by the present procedure differ from those implicitly assumed by Schroeder. It is the functions denoted originally by Schroeder as

$$
\begin{aligned}
&|\Gamma_5[{}^5T_2(t_2^2({}^3T_1)\,e^2({}^3A_2))]\rangle\,,\\
&|\Gamma_4[{}^5T_2(t_2^2({}^3T_1)\,e^2({}^3A_2))]\rangle \qquad (25)
\end{aligned}
$$

both primed and unprimed. The reason for the differences is that there are several possible ways how to distinguish states belonging to repeated irreducible representations. We have chosen the differentiating label β for the two sets of functions $|{}^5T_2\,\Gamma_5\,\beta\rangle$ and $|{}^5T_2\,\Gamma_4\,\beta\rangle$, *viz.* Eq. (25), following the p^n isomorphism of Griffith [18, 19]. Consequently, divergent matrix elements of spin-orbit interaction follow. These have been compiled for future application in the Appendix.

5. Check Between Weak-Field and Strong-Field Calculations. Comparison with Previous Treatments

The complete weak-field and strong-field perturbation matrices differ only by a similarity transformation

$$\mathcal{H}(S, t_{2g}^{m} e_{g}^{n}, \Gamma_j) = \mathbf{U}(\Gamma_j)^{-1}\ \mathcal{H}(S, L, J, \Gamma_j)\ \mathbf{U}(\Gamma_j)\ . \tag{26}$$

In Eq. (26), the transformation matrix $\mathbf{U}(\Gamma_j)$ connects the corresponding energy matrices for irreducible representation Γ_j. Consequently, weak- and strong-field treatments are only parametrically distinct, if complete configuration interaction is included. Upon numerical substitution, identical results should be obtained. Additional checks are provided by a study of the limiting cases where one of the three interactions [*cf.* Eq. (4) and Eq. (5)] is set to zero, since the results expected are well known. All the matrices of the octahedral d^4 configuration were subject to checks for several sets of values of the parameters A, B, C, ζ, and Dq and complete consistency between the results of weak- and strong-field coupling treatments was found. It was demonstrated, in addition, that the matrices of Schroeder [3] produce eigenvalues which are identical to those obtained here. It follows that the previously published [3] strong-field matrices are correct. On the other hand, the weak-field matrices of Dunn and Li [4] may be transformed into real form if corresponding eigenvectors in a row and column are multiplied by i and $-i$, respectively. If the corrections suggested by Krausz [5, 6] are incorporated and an additional error [20] is removed, the matrices thus obtained again produce eigenvalues identical to those of the present treatment.

6. Energy Level Diagrams

The energy levels of d^4 and d^6 electronic configurations in octahedral and tetrahedral ligand fields including both spin-orbit coupling and complete configuration interaction are required in the theory of optical spectra of suitable compounds, particularly at cryogenic temperatures. For application to specific d^4, d^6 complexes, the parameters B, C, ζ, and Dq would be assigned values which best fit the experimental data. In order to make certain qualitative predictions and to discuss the effect of the interactions in a general way, it has proved sufficient to have available energy level diagrams [1, 2] for just one fixed set of values of the parameters. Therefore, numerical values for B, C, ζ, and Dq approximately suitable for hexahydrated complex ions were chosen and the matrices solved. In Fig. 1 we present a diagram for the d^4 electron configuration subject to a field of octahedral symmetry assuming $B = 800\ cm^{-1}$, $C = 4B$, and $\zeta = 290\ cm^{-1}$ (see [21]). The diagram [21] is constructed as function of Dq thus providing the advantage that predictions for complex ions coordinated to ligands of weaker or stronger fields than that of H_2O are possible. The ligand field splitting parameters in tetrahedral and octahedral fields are related by

$$Dq_{tet} = -\tfrac{4}{9} Dq_{oct}\ . \tag{27}$$

Therefore, the same matrices as above may be employed in tetrahedral symmetry as well. The results obtained for the same set of parameters are displayed in Figure 2. The matrices for the octahedral d^6 system may be obtained from those of the original d^4 problem by considering the four electrons as holes. This requires a change of sign for both Dq and ζ. In this way, Fig. 3 and Fig. 4 have been generated where the energy levels for the d^6 electron configuration in fields of octahedral and tetrahedral symmetry are shown [23]. In this case, we have employed $B = 806\ cm^{-1}$, $C = 4B$, and $\zeta = 420\ cm^{-1}$ which values should again correspond approximately to hexaquo ions [24].

The diagrams presented here show the effect of spin-orbit interaction on the various energy terms resulting from the d^4, d^6 configurations [25]. The changes introduced by spin-orbit coupling consist of (i) term splittings which are first-order effects (diagonal matrix elements only) and (ii) term shifts which are of second order (off-diagonal matrix elements). Admittedly, both interactions are small in ions of the first transition metal series considered here. It is expected, however, that these interactions will contribute significantly to the energies in the second and third series. Since the correct matrices for the d^4, d^6 problem are now available, specific applications of the theory are now possible.

In the four situations studied here, *viz.* octahedral and tetrahedral d^4 and d^6 configurations, two different ground states of different spin are formed [26]. The detailed behavior of the levels at this crossover [28] is of interest, since relevant experimental

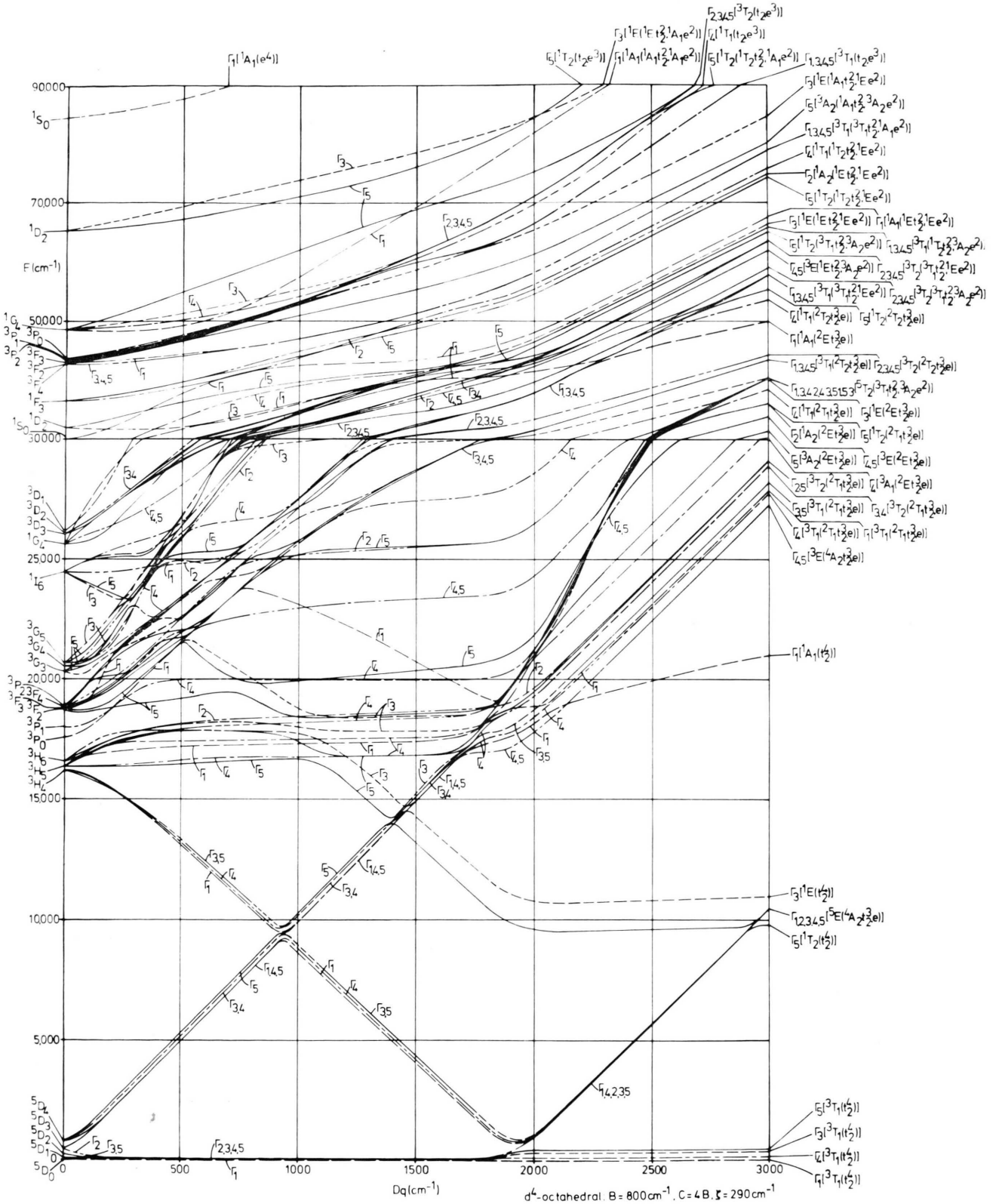

Fig. 1. Energy level diagram for the d^4 configuration in an octahedral field including spin-orbit coupling: $B = 800\ \mathrm{cm}^{-1}$, $C = 4B$, $\zeta = 290\ \mathrm{cm}^{-1}$. The designation of the terms by the strong-field configuration labels and their parent terms corresponds to the largest contribution which is present at a Dq value assumed at the right end of the diagram. The labels have to be supplemented with g subscripts for O_h symmetry.

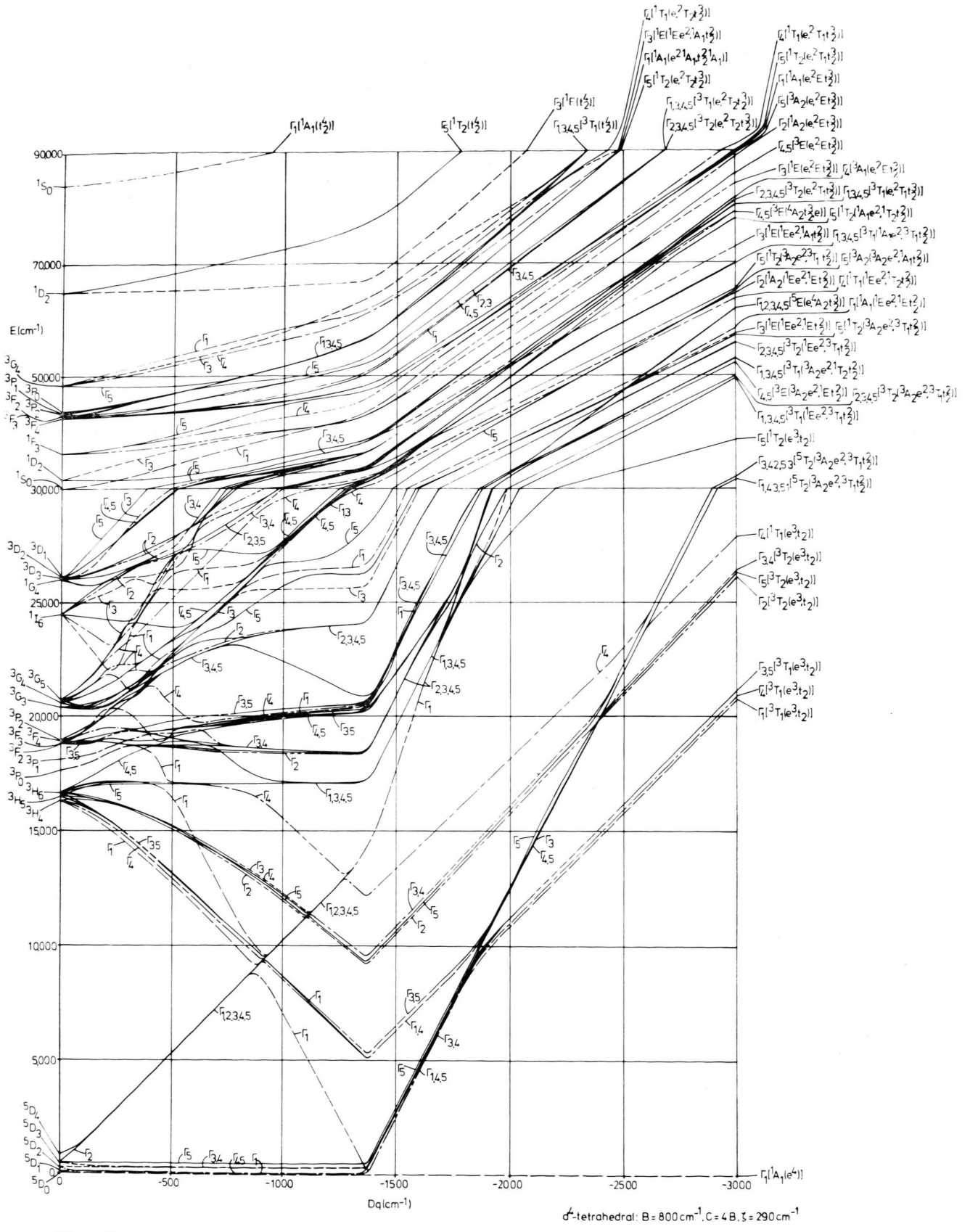

Fig. 2. Energy level diagram for the d^4 configuration in a tetrahedral field including spin-orbit coupling: $B = 800\ \mathrm{cm}^{-1}$, $C = 4\,B$, $\zeta = 290\ \mathrm{cm}^{-1}$. Refer to caption of Fig. 1 for further details.

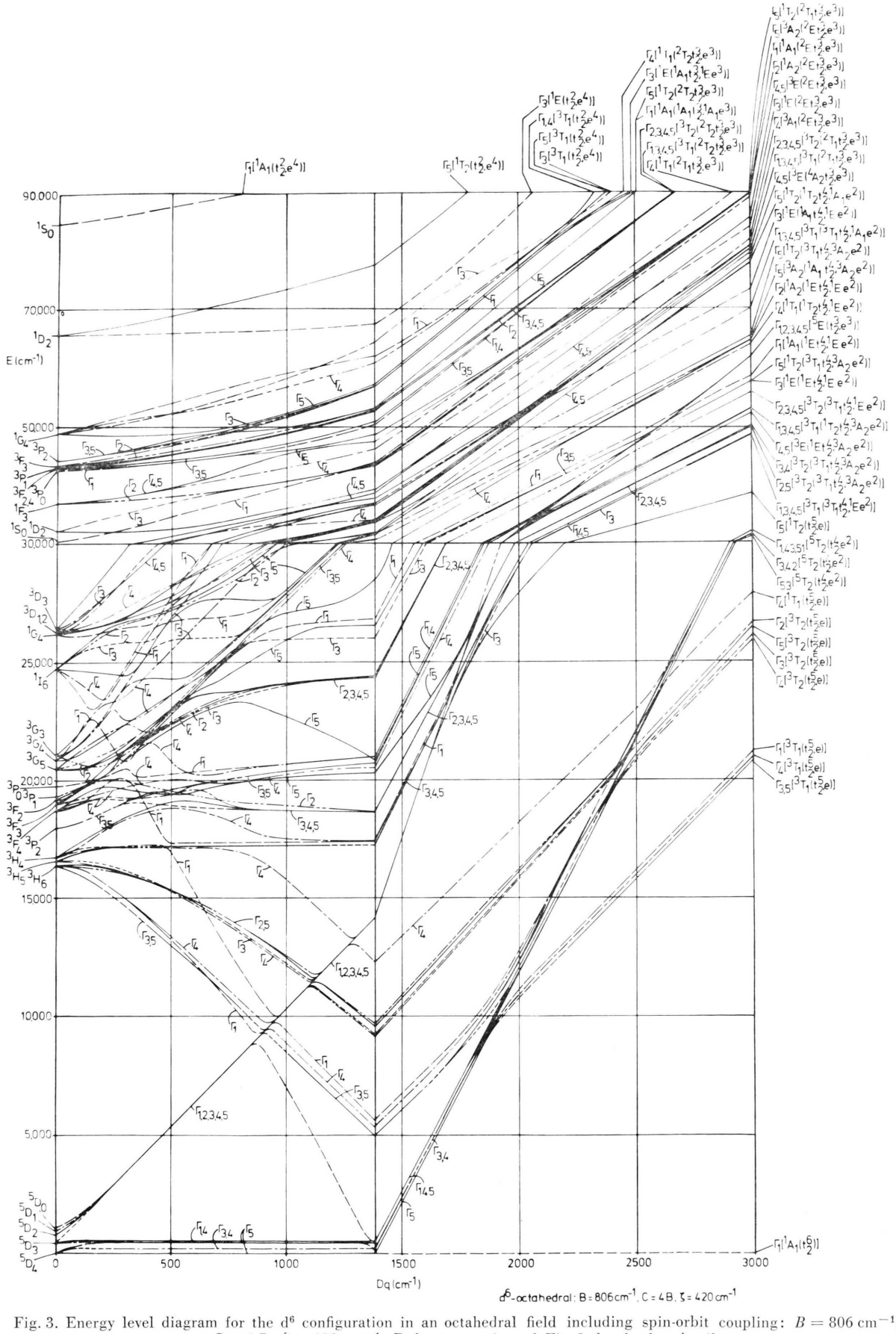

Fig. 3. Energy level diagram for the d^6 configuration in an octahedral field including spin-orbit coupling: $B = 806\ \mathrm{cm}^{-1}$, $C = 4\,B$, $\zeta = 420\ \mathrm{cm}^{-1}$. Refer to caption of Fig. 1 for further details.

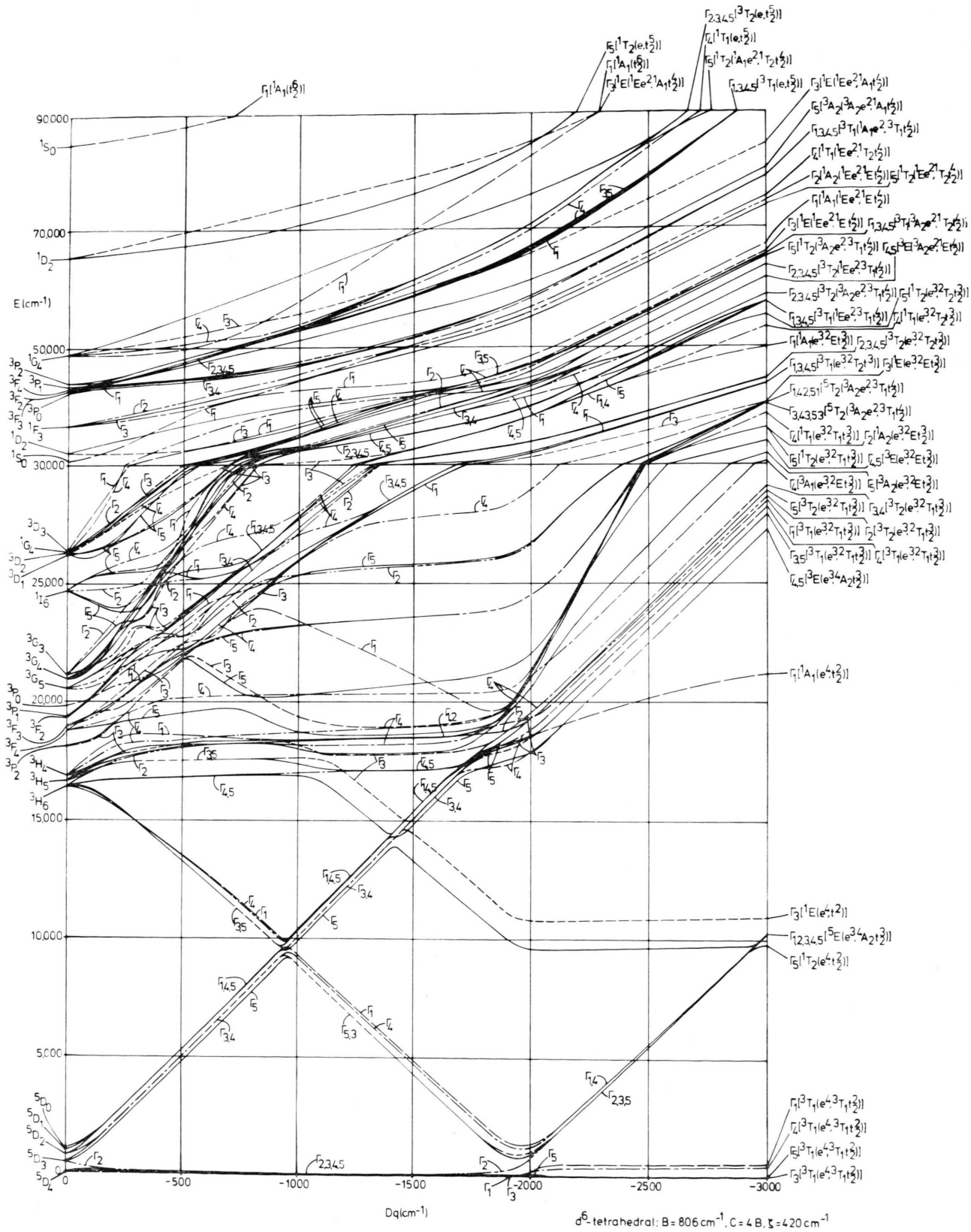

Fig. 4. Energy level diagram for the d^6 configuration in a tetrahedral field including spin-orbit coupling: $B = 806\ \mathrm{cm}^{-1}$, $C = 4\,B$, $\zeta = 420\ \mathrm{cm}^{-1}$. Refer to caption of Fig. 1 for further details.

systems are known [29]. In addition, the present results may provide the starting point for a complete calculation of paramagnetic susceptibilities [30]. This calculation presents magnetic data as function of the semi-empirical spectral parameters B, C, ζ, and $D\,q$ employed here.

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Appendix

Below we list, in units of ζ, matrix elements of spin-orbit coupling which are different from those published by Schroeder [3]. In the tables, i and j number the basis functions in the spin-orbit matrices of Schroeder according to their standard order. For details the reader is refered to the text.

Γ_4: i	j		Γ_5: i	j	
12	2	$\sqrt{6}/4$	13	3	$3\sqrt{10}/20$
12	4	$\sqrt{6}/12$	13	4	$\sqrt{10}/3$
12	5	$-\sqrt{6}/6$	13	5	$-\sqrt{10}/60$
12	6	$-\sqrt{6}/12$	13	6	$\sqrt{10}/30$
12	7	$\sqrt{2}/4$	13	7	$-\sqrt{30}/60$
12	8	$-3\sqrt{2}/4$	13	8	$\sqrt{10}/20$
12	9	$-\sqrt{6}/4$	13	9	$-\sqrt{10}/4$
12	12	1/4	13	10	$-\sqrt{30}/12$
12	13	0	13	13	3/4
12	14	$\sqrt{3}/6$	13	14	0
12	17	$-\sqrt{6}/12$	13	15	$\sqrt{10}/3$
12	18	$-\sqrt{3}/4$	13	16	$-\sqrt{5}/30$
12	21	1/2	13	19	$-\sqrt{30}/60$
12	22	$-\sqrt{3}/2$	13	20	$-\sqrt{15}/12$
13	2	$-\sqrt{3}/2$	13	25	$\sqrt{5}/10$
13	4	$\sqrt{3}/6$	13	26	$-\sqrt{15}/6$
13	5	$-\sqrt{3}/3$	14	3	$-\sqrt{15}/10$
13	6	$\sqrt{3}/3$	14	4	0
13	7	-1	14	5	$-\sqrt{15}/10$
13	8	0	14	6	$\sqrt{15}/5$
13	9	0	14	7	$\sqrt{5}/5$
13	13	$-1/2$	14	8	$-\sqrt{15}/5$
13	14	$\sqrt{6}/6$	14	9	0
13	17	$\sqrt{3}/3$	14	10	0
13	21	$-\sqrt{2}$	14	14	$-1/2$
13	22	0	14	15	0
			14	16	$-\sqrt{30}/10$
			14	19	$\sqrt{5}/5$
			14	20	0
			14	25	$-\sqrt{30}/5$
			14	26	0

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[19] According to this method, the index β is associated with the quantum number J. In the problem at hand, coupling of spin and orbital functions within the $^5T_{2g}$ term produces two spin-orbit functions to each of the irreducible representations Γ_4 and Γ_5. As a consequence of the characterization by $\beta \equiv J$, the spin-orbit matrices contain no off-diagonal elements between the two $^5T_{2g}$ levels labeled Γ_4 or Γ_5. The contribution to the basis function from the corresponding characterizing $^5T_{2g}$ term is then $>98\%$. On the other hand, the approach used by Schroeder [3] gives rise to non-vanishing off-diagonal matrix elements of spin-orbit interaction. In this case, the mixing between the two of each Γ_4 or Γ_5 levels within the $^5T_{2g}$ term amounts to between 50 and 60%.
[20] In the Table IV of the paper by Dunn and Li [4], in addition to the corrections suggested [5, 6] the matrix element $\langle d^4\,{}^1_4\,I_6 \mid \mathcal{H}' \mid d^4\,{}^1_2\,G_4\rangle$ should be listed as follows: $20\,(22)^{1/2}/11\,D\,q$.
[21] A least square fit of the emission spectra [22] of Cr^{2+} and Mn^{3+} ions gave $B = 899\ cm^{-1}$, $C = 3117\ cm^{-1}$ and $B = 1082\ cm^{-1}$, $C = 3916\ cm^{-1}$. The nephelauxetic ratio in $M(H_2O)_6^{n+}$ ions is $\beta \sim 0.88$ if $n = 2$ and $\beta \sim 0.75$ if $n = 3$. The splitting of the free ion ^5D ground term yields $\zeta = 228\ cm^{-1}$ for Cr^{2+} and $\zeta = 348\ cm^{-1}$ for Mn^{3+}. The values chosen are approximate averages of these data.
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[23] The designation of terms in Fig. 1 to Fig. 4 does imply by no means pure configurational states. Indeed, some mixing by CI and spin-orbit interaction is often present and the designation corresponds to the largest contribution at $Dq = 3000\ \mathrm{cm}^{-1}$. For illustration purposes, we give below the percentage content of that eigenfunction which corresponds to the term designation given for the octahedral d^6 configuration in Figure 3.

$45 \pm 2.5\%$: $2\,\Gamma_5\,\{^1T_2[t_2^4(^3T_1)\,e^2(^3A_2)]\}$,
$\Gamma_2\,\{^1E[t_2^3(^2E)\,e^3]\}$,
$\Gamma_1\,\{^1A_1[t_2^4(^1A_1)\,e^2(^1A_1)]\}$.

$50 \pm 2.5\%$: $\Gamma_2, \Gamma_5, \Gamma_4\,\{^3T_1[t_2^4(^3T_1)\,e^2(^1E)]\}$,
$\Gamma_2\,\{^1E[t_2^4(^1A_1)\,e^2(^1E)]\}$,
$\Gamma_2\,\{^1E[t_2^3(^2E)\,e^3]\}$.

$55 \pm 2.5\%$: $\Gamma_1\,\{^3T_1[t_2^4(^3T_1)\,e^2(^1E)]\}$.

$60 \pm 2.5\%$: $\Gamma_2, \Gamma_4, \Gamma_5, \Gamma_1\,\{^3T_1[t_2^4(^1T_2)\,e^2(^3A_2)]\}$,
$\Gamma_2\,\{^1E[t_2^4(^1E)\,e^2(^1E)]\}$,
$\Gamma_5\,\{^1T_2[t_2^3(^2T_2)\,e^3]\}$.

$65 \pm 2.5\%$: $\Gamma_5\,\{^1T_2[t_2^4(^1T_2)\,e^2(^1A_1)]\}$.

The listing is always in the order occuring from lower to higher energies. No listing implies 70% or greater content.

[24] A least square fit of the emission spectrum [22] of the Fe^{2+} ion produces $B = 916\ \mathrm{cm}^{-1}$, $C = 3867\ \mathrm{cm}^{-1}$. There are no data available for the ion Co^{3+} (see [22]). The nephelauxetic ratio $\beta \sim 0.88$ has been assumed [21]. The splitting of the ^5D ground state of Fe^{2+} gives $\zeta = 416\ \mathrm{cm}^{-1}$. The values chosen above are assumed average values.

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[26] In octahedral symmetry and in the d^4 configuration, the change of ground state from ^4E ^5E_g $(t_{2g}^3\ e_g)$ to $^3T_{1g}$ (t_{2g}^4) takes place if $10\,Dq > 6B + 5C + CI$ where CI is the energy of configuration interaction affecting the $^3T_{1g}$ (t_{2g}^4) term only. In the corresponding d^6 configuration, the change of ground state is from $^5T_{2g}$ $(t_{2g}^4 e_g^2)$ to $^1A_{1g}$ (t_{2g}^6) and it occurs if $10\,Dq > 2\frac{1}{2}\,B + 4\,C + CI$ where CI affects alone the $^1A_{1g}$ (t_{2g}^6) term [27]. These crossover energies are affected, in addition, by spin-orbit interaction [28]. In tetrahedral symmetry, the expressions of the conjugate hole configuration have to be employed and Dq has to be replaced by $-\frac{4}{9}\,Dq_{\mathrm{oct}}$.

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