

## Studies of Absorption Spectra

## VIII. Three and More d-Electrons in Cubic Crystal Fields

CHR. KLIXBÜLL JØRGENSEN

*Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark*

The first order splitting of  $d^n$ -terms in relatively weak crystal fields of cubic symmetry is obtained by application of the diagonal sum rule to the intermediate crystal field case, first studied by Bethe. In some of the cases, where the same crystal field quantum number  $\Gamma_n$  applies to two or more levels of the same multiplicity, the method can only give the average value of the term splitting. Terms of  $d^5$ , which are only represented once, cannot show first order splitting in the cubic field.

Bethe<sup>1</sup> found the number of levels, originating from a term with a given  $L$  by group-theoretical means for any type of crystal field symmetry. In the simplest case, the cubic symmetry, the terms of two d-electrons were investigated by Ilse and Hartmann<sup>2</sup>. The present paper gives some of the analogous results for  $d^3$ ,  $d^4$  and  $d^5$ -systems. The splitting of  $d^{10-n}$ -terms is inverted, respectively to the corresponding  $d^n$ -terms. When two or more terms with the same combination of  $L$  and  $S$  occur, or when two levels of the same term have the same<sup>1</sup> crystal field quantum number  $\Gamma_n$ , only the average value of the splitting of the combined levels can be found by this method. As shown below, the splitting of  $D$ - and  $H$ -terms with the same  $S$  cannot be found separately, because of a similar conformity.

In strong crystal fields the levels can be classified<sup>1</sup> according to their number of  $\gamma_3$ - and  $\gamma_5$ -electrons, while they have no fixed  $L$  as the terms in the free ion. Table 1 gives the distribution of the levels for the different electron numbers. The cubic crystal field quantum numbers  $\Gamma_n$  can be found by factorizing the group products of  $\gamma_3$  and  $\gamma_5$  of the occurring electrons\* as linear combinations of the character system of  $\Gamma_n$ , given in Table 1, Ref<sup>1</sup>. The multiplicity  $2S + 1$  of the levels can be found by consideration of the degene-

\* When two or more electrons with the same  $\gamma_n$  are present, their group product must be restricted by Pauli's exclusion principle. This can be done by comparison with the number of terms in the free ion, split by a cubic crystal field, or by comparison with the number of totally non-degenerate states in fields of lower (tetragonal or rhombic) symmetry.

racy number  $(2S + 1)e$ , where  $e = 1, 1, 2, 3, 3$  for  $\Gamma_n$  with  $n = 1, 2, 3, 4, 5$ , respectively. The total sum of degeneracy numbers is given in the last column of Table 1.

The following relation between  $d^{10-n}$ -levels and  $d^n$ -levels can be used for higher numbers of d-electrons:

$$\gamma_5^a \gamma_3^b \equiv \gamma_5^{6-a} \gamma_3^{4-b} \quad (1)$$

Special cases of this analogy to Pauli's equivalence theorem are  $\gamma_5^a \equiv \gamma_5^{6-a}$  and  $\gamma_3^b \equiv \gamma_3^{4-b}$ .

If  $E_1$  is the energy of a  $\gamma_3$ -electron and  $E_2$  of a  $\gamma_5$ -electron, the energy of the  $d^n$ -levels can be written:

$$E = E(\text{free ion}) + NE_1 + (n-N)E_2 \quad (2)$$

It is often convenient to fix the zero-point of the energy scale by defining the energy  $\frac{2n}{5} E_1 + \frac{3n}{5} E_2$  which is constant for all levels of the  $n$  electrons to be = 0, and thus to write:

$$E = E(\text{free ion}) + (N - \frac{2n}{5})(E_1 - E_2) \quad (3)$$

The second part of the expression gives the deviation of the level from the centre of gravity of the term, defined according to Bethe<sup>1</sup>. The Orgel diagram<sup>3</sup> is  $E$  of equ. 3 as function of  $(E_1 - E_2)$ . This parameter indicates the relative strength of the crystal field and is the energy difference between the two states of one d-electron in the same cubic field. In some cases, the value of  $N$  changes from a limiting value for small  $(E_1 - E_2)$  to another value for large  $(E_1 - E_2)$ , as pointed out by Santen and Wieringen<sup>4</sup>. The latter limiting values can be found in Table 1 as the number of  $\gamma_3$ -electrons.

However, in the cases, where only one level  $^{2S+1}\Gamma_n$  occurs in a given electron number in Table 1,  $N$  is invariable for all values of  $(E_1 - E_2)$ . Thus, the  $d^2$ -levels have  $N = 1$  in  $^1\Gamma_4$  and  $^3\Gamma_5$ , corresponding<sup>2</sup> to the first-order values  $E_1 + E_2$  for  $^1G$  and  $^3F$  and  $N = 2$  in  $^3\Gamma_2$  from  $^3F$ . For  $d^3$ -systems is  $N = 0$  in  $^4\Gamma_2$  ( $^4F$ ) and  $N = 1$  in the three cases  $^2\Gamma_1$  ( $^2G$ ),  $^2\Gamma_2$  ( $^2F$ ) and  $^4\Gamma_5$  ( $^4F$ ). For  $d^4$ -systems is  $N = 1$  for  $^3\Gamma_1$  ( $^3G$ ). As also found by Santen and Wieringen<sup>3</sup> is  $N = 1$  for  $^5\Gamma_3$  ( $^5D$ ) and  $N = 2$  for  $^5\Gamma_5$  ( $^5D$ ).

In the cases where two or more  $^{2S+1}\Gamma_n$  are represented, the total number of  $\gamma_3$ -electrons occurring in the levels must equal the total sum of  $N$  for any value of  $(E_1 - E_2)$ . This is analogous to the diagonal sum rule of Condon and Shortley<sup>5</sup>. *E.g.*, in  $d^2$ -systems, the two  $^3\Gamma_4$  have together<sup>2</sup>  $N = \frac{4}{5} + \frac{1}{5} = 1$  and the two  $^1\Gamma_3$  have together  $N = \frac{8}{7} + \frac{6}{7} = 2$ .

The distribution of the  $N$ -sum on the individual levels for  $(E_1 - E_2) \rightarrow 0$  can be found from the theorems of Bethe<sup>1</sup> on the deviations from the centre of gravity of the original term. For  $S$ - and  $P$ -terms, which do not split up in a cubic field,  $N$  is invariably  $\frac{2n}{5}$ . For  $D$ -terms the energy can be expressed:

$$E(\Gamma_3) = E(D) + 3\eta(D) \text{ and } E(\Gamma_5) = E(D) - 2\eta(D) \quad (4)$$

Table 1. Distribution of  $d^n$  levels in strong crystal fields of cubic symmetry.

Electron configuration:	Total sum of degeneracy numbers
d: $\gamma_3$ ${}^2\Gamma_2$	4
$\gamma_5$ ${}^2\Gamma_5$	6
d <sup>2</sup> : $\gamma_3^2$ ${}^1\Gamma_1 + {}^3\Gamma_2 + {}^1\Gamma_3$	6
$\gamma_5\gamma_3$ ${}^1\Gamma_4 + {}^3\Gamma_4 + {}^1\Gamma_5 + {}^3\Gamma_5$	24
$\gamma_5^2$ ${}^1\Gamma_1 + {}^1\Gamma_3 + {}^3\Gamma_4 + {}^1\Gamma_5$	15
d <sup>3</sup> : $\gamma_3^3$ ${}^2\Gamma_2$	4
$\gamma_5\gamma_3^2$ $2{}^2\Gamma_4 + {}^4\Gamma_4 + 2{}^2\Gamma_5$	36
$\gamma_5^2\gamma_3$ ${}^3\Gamma_1 + {}^3\Gamma_2 + 2{}^2\Gamma_3 + 2{}^2\Gamma_4 + {}^4\Gamma_4 + 2{}^2\Gamma_5 + {}^4\Gamma_5$	60
$\gamma_5^3$ ${}^4\Gamma_2 + {}^2\Gamma_2 + {}^2\Gamma_4 + {}^2\Gamma_5$	20
d <sup>4</sup> : $\gamma_3^4$ ${}^1\Gamma_1$	1
$\gamma_5\gamma_3^3$ ${}^1\Gamma_4 + {}^3\Gamma_4 + {}^1\Gamma_5 + {}^3\Gamma_5$	24
$\gamma_5^2\gamma_3^2$ $2{}^1\Gamma_1 + {}^1\Gamma_2 + {}^3\Gamma_2 + 3{}^1\Gamma_3 + {}^3\Gamma_3 + {}^1\Gamma_4 + 3{}^3\Gamma_4 + 3{}^1\Gamma_5 + 2{}^2\Gamma_5 + {}^4\Gamma_5$	90
$\gamma_5^3\gamma_3$ ${}^1\Gamma_1 + {}^3\Gamma_1 + {}^1\Gamma_2 + {}^3\Gamma_2 + {}^1\Gamma_3 + 2{}^2\Gamma_3 + {}^5\Gamma_3 + 2{}^1\Gamma_4 + 2{}^3\Gamma_4 + 2{}^1\Gamma_5 + 2{}^3\Gamma_5$	80
$\gamma_5^4$ ${}^1\Gamma_1 + {}^1\Gamma_3 + {}^3\Gamma_4 + {}^1\Gamma_5$	15
d <sup>5</sup> : $\gamma_5\gamma_3^4$ ${}^3\Gamma_3$	6
$\gamma_5^2\gamma_3^3$ ${}^3\Gamma_1 + {}^3\Gamma_2 + 2{}^2\Gamma_2 + 2{}^2\Gamma_4 + {}^4\Gamma_4 + 2{}^2\Gamma_5 + {}^4\Gamma_5$	60
$\gamma_5^3\gamma_3^2$ $2{}^2\Gamma_1 + {}^4\Gamma_1 + {}^6\Gamma_1 + {}^3\Gamma_2 + {}^4\Gamma_2 + 3{}^1\Gamma_3 + 2{}^4\Gamma_3 + 4{}^2\Gamma_4 + {}^4\Gamma_4 + 4{}^2\Gamma_5 + {}^4\Gamma_5$	120
$\gamma_5^4\gamma_3$ ${}^3\Gamma_1 + {}^3\Gamma_2 + 2{}^2\Gamma_2 + 2{}^2\Gamma_4 + {}^4\Gamma_4 + 2{}^2\Gamma_5 + {}^4\Gamma_5$	60
$\gamma_5^5$ ${}^3\Gamma_3$	6

The parameter  $\eta(D)$  describes thus the splitting of the  $D$ -term and  $E(D)$  =  $E(D$  free ion) +  $\frac{2n}{5} E_1 + \frac{3n}{5} E_2$ . According to Bethe<sup>1</sup>, it is further possible to write for  $F$ -terms and  $G$ -terms:

$$\begin{aligned}
 E(\Gamma_2) &= E(E) + 6\eta(F) & E(\Gamma_1) &= E(G) + 14\eta(G) \\
 E(\Gamma_4) &= E(F) - 3\eta(F) & E(\Gamma_3) &= E(G) + 2\eta(G) \\
 E(\Gamma_5) &= E(F) + \eta(F) & E(\Gamma_4) &= E(G) + 7\eta(G) \\
 & & E(\Gamma_5) &= E(G) - 13\eta(G)
 \end{aligned} \tag{5}$$

The parameters  $\eta$  can be compared with the Lande interval factor  $\zeta$  for multiplet splitting<sup>5</sup> due to coupling between  $L$  and  $S$ .

When equ. 5 is applied to the case of  ${}^2\Gamma_4$  in  $d^3$ -systems (or  ${}^3\Gamma_4$  in  $d^4$ -systems) by use of the known values of  $\eta(F)$  and  $\eta(G)$ , it can be concluded that the splitting of  $H$ -terms is of the form

$$\begin{aligned}
 \text{average of two } E(\Gamma_3) &= E(H) + 3\eta(H) \\
 E(\Gamma_4) &= E(H) \\
 E(\Gamma_5) &= E(H) - 2\eta(H)
 \end{aligned} \tag{6}$$

Since similar results are not known for  $I$ -terms,  $S = 0$  has not yet been treated in  $d^4$ -systems by the present method.

Table 2. Multiplet splitting factors  $\eta(L)$  of systems with two, three\* and four *d*-electrons, expressed in units of  $(E_1 - E_2)$ .

$d^2$	<i>S</i>	$d^3$	<i>S</i>	$d^4$	<i>S</i>
$\eta(D) = +4/35$	0	$2\eta(D_{av}) + \eta(H) = +8/105$	$1/2$	$\eta(D) = -1/5$	2
$\eta(F) = +1/5$	1	$\eta(F) = -1/5$	$3/2$	$\eta(D) + \eta(H) = -5/21$	1
$\eta(G) = +1/35$	0	$\eta(F) = -1/30$	$1/2$	$2\eta(F_{av}) = -1/60$	1
		$\eta(G) = -1/70$	$1/2$	$\eta(G) = -3/70$	1

\* Finkelstein and Van Vleck<sup>11</sup> have given the matrices for  $d^3$  in cubic fields.  $\eta(H)$  is separately  $\frac{1}{15}(E_1 - E_2)$  and  $\eta$  of the two  ${}^2D$ -terms  $\frac{1}{10}$  and  $\frac{-19}{210}$ , giving the sum in Table 2. The first-order deviations of the two  $\Gamma_4({}^2H)$  levels are given<sup>11</sup> as  $\pm 0.261(E_1 - E_2)$  which is an energy of the same order of magnitude as the non-diagonal elements in the matrices.

Equ. 6 has the interesting consequence that only the sum  $\eta(D) + \eta(H)$  can be determined by this method in cases where *D*- and *H*-terms have the same *S*, since  $\eta(D)$  and  $\eta(H)$  only occur in proportional equations. This is connected with the fact that the character systems can be written

$$C(H) = 2C(P) + C(D) \quad (7)$$

This is not a sufficient cause for the peculiar degeneracy of equ. 6. Thus the expression

$$C(G) = C(S) + C(P) + C(D) \quad (8)$$

has no significant effect of the energy expressions. Generally the character systems can be written as a linear combination with the coefficients  $A_n \geq 0$  of only four (and not five) fundamental character systems:

$$C(L) = A_0C(S) + A_1C(P) + A_2C(D) + A_3C(F) \quad (9)$$

Thus, the number of  $\Gamma_i$  levels at a given *L* is always equal to  $A_2 + A_3$ , the sum of  $\Gamma_2$  and  $\Gamma_3$  levels.

The results of Table 2 are obtained from the diagonal sum arguments above and equations 4—6. The subscript "av" denotes the average energy of the terms in the cases where two terms with the same combination of *L* and *S* are found in the free ion<sup>5</sup>.

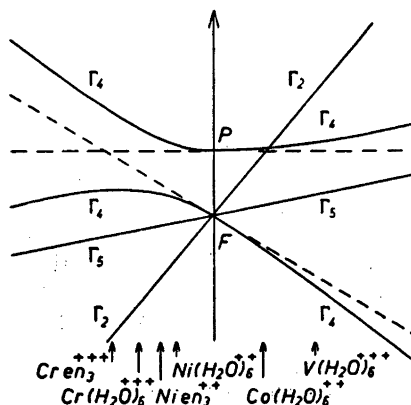


Fig. 1. Orgel diagram for terms of highest multiplicity in cubic crystal fields. Left-hand side  $d^2$ - and  $d^3$ -systems in octahedral complexes with negative ions or dipoles as ligands. Right-hand side  $d^2$ - and  $d^3$ -systems.

When the method is applied to  $d^5$ , all the  $\eta(L)$  are 0. This could also be inferred from the inversion of the first order term splittings in  $d^{10-n}$  relative to  $d^n$ , since  $d^5$  is its own hole-equivalent. The observed splittings<sup>6</sup> of  $^4G$  in  $Mn^{++}$  and  $Fe^{+++}$  are thus due to second order effects of  $(E_1 - E_2)$  in stronger crystal fields (here acting on  $^4\Gamma_4$  and  $^4\Gamma_5$  for the two first bands). Since these terms usually have only small distances in the free ions with  $d^3$ ,  $d^4$  and  $d^5$ -configurations, their interaction can be described by the non-diagonal elements in the matrix of the form given by Orgel<sup>6</sup> which are presumably quite prominent for  $S$  smaller than the maximum value.  $E$  (free ion) of equ. 3 is also intermixed of the different interacting states, originating in the weak crystal field.

As an example of the transition from weak to strong crystal fields, Fig. 1 illustrates the interaction of levels with the same  $\Gamma_n$  in the case where the highest multiplicity is represented by  $F$ - and  $P$ -terms. The right-hand side is the Fig. 3 of Ref.<sup>3</sup>, valid for  $d^2$  and  $d^7$ , while the left-hand side applies to  $d^3$  and  $d^8$  in octahedral complexes<sup>4</sup>. Some concrete examples of crystal field strengths are given by the vertical arrows. The corresponding observed wave numbers are given in Table 3. It is seen that  $\Gamma_5(F)$  is lower in  $d^3$  and  $d^8$ -systems than the lowest of the two  $\Gamma_4$ . At high values of  $(E_1 - E_2)$ ,  $\Gamma_4$  should in these systems be placed a constant amount below  $\Gamma_5$  according to Orgel<sup>3</sup>. This is supported by the tetragonal splitting of the first band of mono- and trans-disubstituted chromium(III) complexes, since  $\Gamma_4$  has first order tetragonal effects in contrast to  $\Gamma_5$ . Nevertheless, a crossing of  $\Gamma_4$  and  $\Gamma_5$  seems highly improbable. Rather the wave-functions are intermixed<sup>1</sup> by passing from weak to strong crystal fields. The third band in chromium(III) complexes, corresponding to the transition to the highest  $\Gamma_4$  is predicted far in the ultra-violet.

Table 3. Maxima of observed absorption bands in  $cm^{-1}$ .

Shoulders are given in parenthesis. "en" = ethylenediamine. The energy difference between the  $P$  and  $F$  term of highest multiplicity is given for the free ion, known from atomic spectroscopy<sup>10</sup>.

V $(H_2O)_6^{+++}$	17 300	25 800			$^3P - ^3F = 13 300$
Cr $(H_2O)_6^{+++}$	17 400	24 500			$^4P - ^4F = 14 200$
Cr en <sub>3</sub> <sup>+++</sup>	21 850	28 450			— —
Co $(H_2O)_6^{++}$	8 000	(16 000)	19 400	(21 550)	$^4P - ^4F = 15 400$
Ni $(H_2O)_6^{++}$	8 000	13 500	(15 400)	25 300	$^3P - ^3F = 16 900$
Ni en <sub>3</sub> <sup>++</sup>	11 200	18 350		29 000	— —

Analogous to the generalization from the  $d^2$ -levels to most of the  $d^n$ -levels in cubic crystal fields, Ballhausen and the author will publish elsewhere<sup>12</sup> results on  $d^n$ -levels in crystal fields of tetragonal and rhombic symmetry. These will utilize the calculations on one and two d-electrons in fields of low symmetry, according to Ballhausen<sup>7, 8, 9</sup>, where the electron distributions in strong crystal fields on the individual tetragonal and rhombic quantum numbers  $\gamma_n$  can also be connected with the energy expressions in weak crystal fields of the corresponding symmetry for most  $d^n$ -systems.

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