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d-Electrons in Crystal Fields of Different Symmetries

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BETHE¹ calculated the number of possible energy levels originating from an electron with a given l in crystal fields of any symmetry. These results apply also to an atomic term with given L in crystal fields of intermediate strength. Small letters are used in this paper to denote single electrons (l , γ_n , etc.) and capital letters to designate total systems (L , Γ_n , etc.). Quantitative calculations of the energy differences occurring in the complex ions of the first transition group were first performed by ILSE and HARTMANN.^{2,3} These authors applied the theory to Ti^{+3} and V^{+3} . Similar calculations have recently been reported for Cu^{++} , Ni^{++} , and most of the other metal ions of the first transition group.⁴⁻⁷ The theory of d^2 -levels in crystal-fields of cubic symmetry³ has been extended to d^n -levels in such fields.⁷ The present paper gives a similar treatment of d^n -levels in fields of lower symmetry (tetragonal and rhombic, the latter being the lowest symmetry of consequence for the splitting of the levels), based on the calculations^{4,5} on d and d^2 -levels in these fields.

Introduction.

The character system of a state in a crystal field of given symmetry can be considered as a p -dimensional vector, if p different numbers are given in the set, e. g. $p = 5$ in the cubic case, where the character systems C are given as the sets (e , c_2 , c_3 , c_4 , c_5). In this five-dimensional space, five fundamental vectors are given as the "irreducible Darstellungen" of BETHE (ref. 1, Table 1). The characters are here given in the order of BETHE.¹ (In the textbook of EYRING, WALTER and KIMBALL²⁸ the characters are given in the order (e , c_5 , c_2 , c_3 , c_4) in the cubic while BETHE's order is not changed in the tetragonal case) They correspond to the quantum numbers Γ_n :

$$\left. \begin{aligned} C(I_1) &= (1, 1, 1, 1, 1) \\ C(I_2) &= (1, 1, -1, -1, 1) \\ C(I_3) &= (2, 2, 0, 0, -1) \\ C(I_4) &= (3, -1, 1, -1, 0) \\ C(I_5) &= (3, -1, -1, 1, 0). \end{aligned} \right\} \quad (1)$$

Any non-fundamental vector C can be expressed as a linear combination of the fundamental vectors in only one way:

$$C = a_1 C(I_1) + a_2 C(I_2) + a_3 C(I_3) + a_4 C(I_4) + a_5 C(I_5). \quad (2)$$

The linear combination coefficients a_n of eq. 2 are always positive integers.

The character systems $C(L)$ found by BETHE by considerations of the single $(2L + 1)$ -dimensional rotation group can be expressed in the familiar tables of cubic term splittings:

$$\left. \begin{aligned} C(S) &= C(I_1) \\ C(P) &= C(I_4) \\ C(D) &= C(I_3) + C(I_5) \\ C(F) &= C(I_2) + C(I_4) + C(I_5) \\ C(G) &= C(I_1) + C(I_3) + C(I_4) + C(I_5) \\ C(H) &= C(I_3) + 2C(I_4) + C(I_5), \end{aligned} \right\} \quad (3)$$

where S, P, D is the usual spectroscopic notation for $L = 0, 1, 2, \dots$. This table was first given by BETHE, and extended for some higher values of L by HELLWEGE.⁸ It is periodical¹ with $L = 12$ (λ is a positive integer)

$$C(12\lambda + L) = \lambda C_{12} + C(L), \quad (4)$$

where $C_{12} = (24, 0, 0, 0, 0) = C(I_1) + C(I_2) + 2C(I_3) + 3C(I_4) + 3C(I_5)$.

An important operation is the formation of internal vector products from the vectors (e, c_2, c_3, c_4, c_5) and $(e', c'_2, c'_3, c'_4, c'_5)$, viz.

$$C = (e e', c_2 c'_2, c_3 c'_3, c_4 c'_4, c_5 c'_5). \quad (5)$$

These products C can also be expressed in the fundamental vectors of eq. 1, giving the results of Table 1. This is a multiplication table of Γ_p and Γ_q , showing the validity of the commutative law:

TABLE 1. Internal vector products in cubic symmetry.

| | Γ_1 | Γ_2 | Γ_3 | Γ_4 | Γ_5 |
|------------------------------|------------|------------|----------------------------------|---|---|
| $\Gamma_1 \dots \dots \dots$ | Γ_1 | Γ_2 | Γ_3 | Γ_4 | Γ_5 |
| $\Gamma_2 \dots \dots \dots$ | Γ_2 | Γ_1 | Γ_3 | Γ_5 | Γ_4 |
| $\Gamma_3 \dots \dots \dots$ | Γ_3 | Γ_3 | $\Gamma_1 + \Gamma_2 + \Gamma_3$ | $\Gamma_4 + \Gamma_5$ | $\Gamma_4 + \Gamma_5$ |
| $\Gamma_4 \dots \dots \dots$ | Γ_4 | Γ_5 | $\Gamma_4 + \Gamma_5$ | $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$ | $\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$ |
| $\Gamma_5 \dots \dots \dots$ | Γ_5 | Γ_4 | $\Gamma_4 + \Gamma_5$ | $\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$ | $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$ |

In crystal fields of tetragonal symmetry the character systems are also five-dimensional vectors, and there are five fundamental vectors $C(\Gamma_{t1})$, $C(\Gamma_{t2})$, $C(\Gamma_{t3})$, $C(\Gamma_{t4})$, and $C(\Gamma_{t5})$ with the coordinates given in ref. 1, Table 5. It is seen that the first coordinate, e , is 1, 1, 1, 1, 2, respectively. This is normally called the degeneracy number of the state, analogous to e in the cubic case. We shall here denote cubic quantum numbers by Γ_{cn} (or simply Γ_n where no misunderstanding is possible), tetragonal numbers by Γ_{tn} and rhombic ones by Γ_{rn} .

The tetragonal character systems of L , $C(L)$ are given in ref. 1, Table 6. On the analogy of eq. 4, $C(L)$ is periodical¹ with the period 4, i. e.

$$\left. \begin{aligned} C(4\lambda + L) &= \lambda C_4 + C(L) \\ C_4 &= C(P) + C(D) = C(S) + C(F). \end{aligned} \right\} \quad (6)$$

Since C_4 is thus expressible, all tetragonal $C(L)$ can be expressed as linear combinations of $C(S)$, $C(P)$, $C(D)$, and $C(F)$ with non-negative coefficients. This is the cause of the similar behaviour⁷ of a cubic $C(L)$ vector when the following arguments are considered.

The values of tetragonal $C(L)$ can be found from eq. 6 and 7:

$$\left. \begin{aligned} C(S) &= C(\Gamma_{t1}) \\ C(P) &= C(\Gamma_{t2}) + C(\Gamma_{t5}) \\ C(D) &= C(\Gamma_{t1}) + C(\Gamma_{t3}) + C(\Gamma_{t4}) + C(\Gamma_{t5}) \\ C(F) &= C(\Gamma_{t2}) + C(\Gamma_{t3}) + C(\Gamma_{t4}) + 2C(\Gamma_{t5}). \end{aligned} \right\} \quad (7)$$

It is now of great interest to know whether a certain cubic state Γ_{cn} can be identified with certainty as a sum of tetragonal states Γ_{tm} . This corresponds to the effects of making a cubic crystal-field very slightly tetragonal and thus forming tetragonal splittings of the cubic levels. Eq. 3 and 7 give the two only possible solutions:

$$\left. \begin{array}{ll} \text{Possibility 1} & \text{Possibility 2} \\ \Gamma_{c1} \rightarrow \Gamma_{t1} & \Gamma_{c1} \rightarrow \Gamma_{t1} \\ \Gamma_{c2} \rightarrow \Gamma_{t3} & \Gamma_{c2} \rightarrow \Gamma_{t4} \\ \Gamma_{c3} \rightarrow \Gamma_{t1} + \Gamma_{t3} & \Gamma_{c3} \rightarrow \Gamma_{t1} + \Gamma_{t4} \\ \Gamma_{c4} \rightarrow \Gamma_{t2} + \Gamma_{t5} & \Gamma_{c4} \rightarrow \Gamma_{t2} + \Gamma_{t5} \\ \Gamma_{c5} \rightarrow \Gamma_{t3} + \Gamma_{t4} & \Gamma_{c5} \rightarrow \Gamma_{t3} + \Gamma_{t5}. \end{array} \right\} \quad (8)$$

BETHE chose possibility 1, but this cannot be done exclusively on the basis of these equations.

From the internal vector products, Table 2 can be constructed by methods similar to those outlined above for Table 1:

TABLE 2. Internal vector products in tetragonal symmetry.

| | Γ_{t1} | Γ_{t2} | Γ_{t3} | Γ_{t4} | Γ_{t5} |
|---------------------|---------------|---------------|---------------|---------------|---|
| Γ_{t1} | Γ_{t1} | Γ_{t2} | Γ_{t3} | Γ_{t4} | Γ_{t5} |
| Γ_{t2} | Γ_{t2} | Γ_{t1} | Γ_{t4} | Γ_{t3} | Γ_{t5} |
| Γ_{t3} | Γ_{t3} | Γ_{t4} | Γ_{t1} | Γ_{t2} | Γ_{t5} |
| Γ_{t4} | Γ_{t4} | Γ_{t3} | Γ_{t2} | Γ_{t1} | Γ_{t5} |
| Γ_{t5} | Γ_{t5} | Γ_{t5} | Γ_{t5} | Γ_{t5} | $\Gamma_{t1} + \Gamma_{t2} + \Gamma_{t3} + \Gamma_{t4}$ |

Table 2 gives no reason for preferring possibility 1 of eq. 8 to possibility 2, since it is exactly symmetrical with respect to change of Γ_{t3} to Γ_{t4} et vice versa.

In the rhombic case all the four fundamental vectors have $e = 1$, i. e. they are all only once degenerate. According to BETHE,

they are connected with the tetragonal quantum numbers in the following way:

$$\left. \begin{aligned} \Gamma_{t1} &\rightarrow \Gamma_{r1} \\ \Gamma_{t2} &\rightarrow \Gamma_{r2} \\ \Gamma_{t3} &\rightarrow \Gamma_{r1} \\ \Gamma_{t4} &\rightarrow \Gamma_{r2} \\ \Gamma_{t5} &\rightarrow \Gamma_{r3} + \Gamma_{r4} \end{aligned} \right\} \quad (9)$$

They have thus the following multiplication table:

TABLE 3. Internal vector products in rhombic symmetry.

| | Γ_{r1} | Γ_{r2} | Γ_{r3} | Γ_{r4} |
|---------------------|---------------|---------------|---------------|---------------|
| Γ_{r1} | Γ_{r1} | Γ_{r2} | Γ_{r3} | Γ_{r4} |
| Γ_{r2} | Γ_{r2} | Γ_{r1} | Γ_{r4} | Γ_{r3} |
| Γ_{r3} | Γ_{r3} | Γ_{r4} | Γ_{r1} | Γ_{r2} |
| Γ_{r4} | Γ_{r4} | Γ_{r3} | Γ_{r2} | Γ_{r1} |

Crystal Fields in Co-Ordination Compounds.

From the formulae in ref. 4, it is easily shown that in octahedral complexes the crystal field energy levels are determined only by three quantities which represent the perturbations from the sets of two ligands on each of three axes in the Cartesian coordinate system. This is an extension of the equivalence of *z*-axis contributions, applied to copper (II) complexes,⁴ and in accord with the empirical observations of SUEDA,⁹ that the absorption spectrum is determined only by the influences of the three sets of ligands in *trans*-positions.

In the following calculations the distances of all the ligands are assumed to be equal, giving the same values when put in the functions⁴ B_2 and B_4 . However, the following considerations are also valid when different values of B_2 and B_4 are obtained from each of the ligands. The difference between the six ligands is expressed as differences in the effective point dipole moment μ , but the results can be applied to ionic charges q , G_2 and G_4 .

as well. The sum of the dipoles in the direction of the x -axis and y -axis and z -axis are represented by μ_1 , μ_2 , and μ_3 .

The complex is said to have a crystal-field of cubic symmetry, if $\mu_1 = \mu_2 = \mu_3$. If two of the dipole moment sums are equal, but different from the third, e. g. $\mu_1 = \mu_2 \neq \mu_3$, the crystal field has tetragonal symmetry. Whenever all the three are different, one has rhombic symmetry, which is the lowest symmetry possible in any octahedral complex.

The energy E of a given level is expressed formally as

$$\left. \begin{aligned} E &= E(\text{free ion}) + E(\text{common pert.}) \\ &+ E(\text{cub}) + E(\text{tetr}) + E(\text{rhomb}). \end{aligned} \right\} \quad (10)$$

$E(\text{free ion})$ is the energy of the corresponding atomic term, which is perturbed by the crystal field (by interaction between different terms the intermixed sum of the individual $E(\text{free ion})$). $E(\text{common pert.})$ is the energy equal for all levels of the electron configuration due to the B_0 contributions of the perturbation. $E(\text{cub})$ is the energy of the corresponding cubic and $E(\text{tetr.})$ of the corresponding tetragonal level (see the splitting rules eq. 8 (Poss. 1) and eq. 9), and finally $E(\text{rhomb})$ the remaining energy, which is only different from 0 in Γ_{t5} -levels, split to Γ_{r3} and Γ_{r4} , and in the interacting two Γ_{r1} states. The latter result is shown in what follows to be connected with Bethe's theorem of the centre of gravity of a group of levels whose degeneracy is removed by fields of less symmetry. B_0 is not regarded at all, because it only contributes to $E(\text{common pert.})$. B_2 occurs alone in $E(\text{tetr.})$, and $E(\text{rhomb})$, while B_4 occurs in all the three last parts of eq. 10. In crystal fields of cubic symmetry, $E(\text{tetr.}) = E(\text{rhomb}) = 0$.

In the complex ions with six equal molecules as ligands, the crystal field does not a priori need being of cubic symmetry since the ligands may have slightly differently induced dipole moment and distances. Eq. 10 would give decreased energy if $E(\text{tetr.})$ and $E(\text{rhomb})$ can be negative, i. e. some tetragonal or rhombic splitting of the ground-state occurs. VAN VLECK¹⁰ pointed out early that the Jahn-Teller effect would only allow complex ions to be stable in which the ground-state is only once degenerate on a $(2L + 1)$ basis, i. e. $e = 1$ in the corresponding

vector. The only stable octahedral complexes of cubic symmetry thus have T_1 or T_2 as ground-states, while the others deform to tetragonal or even rhombic symmetry (in the case of T_{15}). However this theorem concerns only the direction of deformation, not the absolute deviation from cubic symmetry.

The ground-states in most magnetically anomalous ions (with the total spin quantum number S less than the S in the free ion) are T_{e1} (in $d^5 T_{e5}$), while the magnetically normal ions with the maximum value of S are distributed in the following way in octahedral complexes:

$$\left. \begin{array}{l} d \text{ and } d^6 \text{ rhombic or "compressed" tetragonal} \\ d^2 \text{ and } d^7 \text{ tetragonal} \\ d^3 \text{ and } d^8 \text{ cubic} \\ d^4 \text{ and } d^9 \text{ tetragonal} \\ d^5 \text{ cubic.} \end{array} \right\} \quad (11)$$

VAN VLECK¹⁰ has maintained that systems with one d -electron have the least energy when they have rhombic symmetry. As is seen in the following section, tetragonal symmetry with $\mu_1 > \mu_2 = \mu_3$ would also give a stable once degenerate ground-state. The "compressed" tetragonal form of the complex would probably have approximately the same energy as the rhombic form. Therefore it is possible that the titanium (III) hexa-aquo ion exists in an equilibrium between the two forms. Whenever tetragonality of the type $\mu_1 = \mu_2 > \mu_3$ is stable as in d^4 - and d^9 -systems (e. g. chromium (II) or copper (II) complexes), this structure will be energetically favoured because the ligands are held in place by the steeply increasing potential of the sphere-symmetrical kernel. The tetragonality can thus be due only to weakening of some of the electrostatic bonds to the ligands. This is more likely to happen for two of the six ligands rather than for four as in the case of "compressed" tetragonality.

Two Interacting States in Crystal Fields of Intermediate Strength.

When a given combination of S and Γ_n is represented only once in an electron configuration, its energy will be linearly dependent on crystal field strength (in cubic fields $(E_1 - E_2)$, where E_1 is the energy of a γ_3 -electron and E_2 the energy of a γ_5 -electron). This dependence is found by calculations on either weak or strong crystal fields. The two latter terms are defined in the following way: In weak fields $(E_1 - E_2)$ is negligibly small, compared with the distances between terms of different L in the free ion. In the strong fields $(E_1 - E_2)$ is much larger than these distances.

When two or more levels with the same S and Γ_n occur, the weak and strong crystal fields may give totally different energy expressions. In the case of cubic symmetry the values of N in systems with n d -electrons correspond to the number of γ_3 -electrons. We define:

$$E(\text{cub}) = \left(N - \frac{2n}{5}\right)(E_1 - E_2). \quad (12)$$

In weak fields N is not always an integer and in strong fields the original terms with definite values of L can no longer be distinguished. The diagonal sum rule only ensures⁷ that the sum $N_1 + N_2 + \dots + N_q$ of the q different levels is constant for each value of the crystal field, corresponding to varying intermixing of the strong-field wave-functions.

ORGEL¹¹ determined this interaction in a very important case: the two Γ_4 originating in weak crystal fields from 3F and 3P in d^2 -systems, and going to γ_5^2 and γ_3^2 in strong crystal fields. The numerical result can as well be applied⁷ to the two Γ_4 of highest S in d^3 -, d^7 -, and d^8 -systems. In what follows, the interaction between two states is generally treated without use of Condon-Shortley parameters. The energy of the two states in intermediate crystal field strength can be found as the two roots E in the matrix of second order¹¹

$$\begin{vmatrix} E_\alpha + \left(N_\alpha - \frac{2n}{5}\right)(E_1 - E_2) - E & K \\ K & E_\beta + \left(N_\beta - \frac{2n}{5}\right)(E_1 - E_2) - E \end{vmatrix} = 0. \quad (13)$$

K is the energy of interaction between the two states considered. N_α and N_β are the integers corresponding to the strong crystal field case. In the free ion ($E_1 - E_2$) equals 0. Here the two energy roots are E_a and E_b :

$$\left. \begin{matrix} E_a \\ E_b \end{matrix} \right\} = \frac{E_\alpha + E_\beta}{2} \pm \sqrt{\left(\frac{E_\alpha - E_\beta}{2}\right)^2 + K^2}. \quad (14)$$

It is seen that E_α and E_β always occur in the closed interval between E_a and E_b . It is thus possible to choose a parameter x , such that

$$\left. \begin{aligned} 0 &\leq x \leq 1 \\ E_\alpha &= (1-x)E_a + xE_b \\ E_\beta &= xE_a + (1-x)E_b. \end{aligned} \right\} \quad (15)$$

Eq. 14 and 15 then gives

$$K^2 = x(1-x)(E_b - E_a)^2. \quad (16)$$

The parameters x and $(1-x)$ chosen in eq. 15 are just the intermixing coefficients¹⁶ of the strong field-states in the states in the weak field. This relation is biunique in the case of only two interacting states, found for instance in d^2 -levels in cubic fields. In d^8 -systems, $(1-x)$ is to be substituted for x in Table 4. The data are compiled in Table 4. Two interacting states have

TABLE 4. Interacting states among d^2 -levels in crystal fields of cubic symmetry.

| Quantum number | E_a | E_b | x | $\left(\frac{K}{E_b - E_a}\right)^2 = x - x^3$ | States in strong crystal fields |
|-----------------|---------|---------|-------|--|----------------------------------|
| 3T_4 | 3F | 3P | $1/5$ | $4/25$ | $\gamma_5^2 + \gamma_5 \gamma_3$ |
| 1T_1 | 1G | 1S | $3/5$ | $6/25$ | $\gamma_5^2 + \gamma_3^2$ |
| 1T_3 | 1D | 1G | $4/7$ | $12/49$ | $\gamma_5^2 + \gamma_3^2$ |
| 1T_5 | 1D | 1G | $4/7$ | $12/49$ | $\gamma_5^2 + \gamma_5 \gamma_3$ |

the smallest energy difference when the diagonal elements of eq. 13 are equal, and then it is $2K$. Since the interaction energy K has nearly its maximum value, $\frac{1}{2}(E_b - E_a)$, for the three d^2 -sets

with $S = 0$, their minimum distance must occur at very small crystal-field strengths, i. e. the second-order effects in $(E_1 - E_2)$ are in most cases more important than the first-order effects found in weak cubic fields. The asymptotes in strong crystal fields are given by the equations

$$E = E_a + \left(N_a - \frac{2n}{5}\right)(E_1 - E_2)$$

and the analogous with E_β and N_β .

One d -Electron Systems.

As mentioned above, the 2D -state of one d -electron is split up in fields of lower symmetry as shown in Fig. 1.

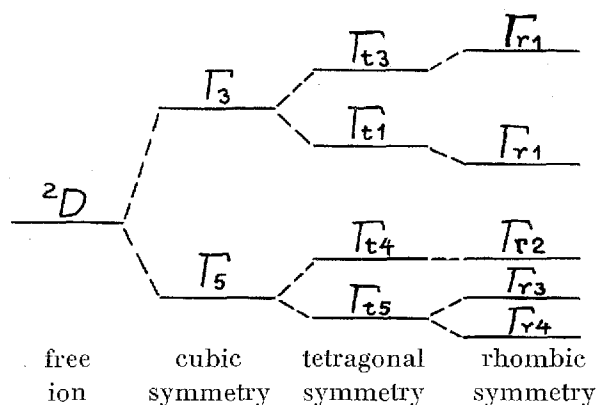


Fig. 1. States of one d -electron in octahedral complexes of decreasing symmetry.

BALLHAUSEN⁴ calculated the energies of the rhombic symmetry. (In all the following equations, the factor $\frac{8}{45}f^2$ is omitted for convenience). The three lowest states have:

$$\left. \begin{aligned} &\Gamma_{e5} \rightarrow \Gamma_{t4} \rightarrow \Gamma_{r2}: \\ &\mu_1 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] + \mu_2 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] + \mu_3 \left[-\frac{2}{7} B_2 + \frac{1}{21} B_4 \right] \\ &\Gamma_{e5} \rightarrow \Gamma_{t5} \rightarrow \Gamma_{r3}: \\ &\mu_1 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] + \mu_2 \left[-\frac{2}{7} B_2 + \frac{1}{21} B_4 \right] + \mu_3 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] \end{aligned} \right\} \quad (17)$$

$$\left. \begin{aligned} & \Gamma_{c5} \rightarrow \Gamma_{t5} \rightarrow \Gamma_{r4}: \\ & \mu_1 \left[-\frac{2}{7} B_2 + \frac{1}{21} B_4 \right] + \mu_2 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] + \mu_3 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right]. \end{aligned} \right\} \quad (17)$$

The affiliation to tetragonal states can be found by putting $\mu_1 = \mu_2$. In the limit, where $\mu_1 = \mu_2 = \mu_3$, the cubic states are found. The rhombic quantum numbers Γ_{r3} and Γ_{r4} are chosen arbitrarily. The energies of the two highest states are roots of the equation

$$\left. \begin{aligned} & E^2 - (H_{22} + H_{2-2} + H_{00}) E + (H_{22} H_{00} \\ & + H_{2-2} H_{00} - 2(H_{20})^2) = 0, \end{aligned} \right\} \quad (18)$$

giving a square-root dependence. The functions H_{ab} are defined in ref. 4. Only in the case $\mu_1 = \mu_2$ is the dependence on crystal field strength linear, because H_{20} then equals 0. This represents the interaction between the two states with the same rhombic quantum number Γ_{r1} .

In the tetragonal case $\mu_1 = \mu_2$, these two states are normal, and the four possible states are:

$$\left. \begin{aligned} & \Gamma_{c3} \rightarrow \Gamma_{t3}: 2 \mu_1 \left[\frac{1}{7} B_2 + \frac{19}{84} B_4 \right] + \mu_3 \left[-\frac{2}{7} B_2 + \frac{1}{21} B_4 \right] \\ & \Gamma_{c3} \rightarrow \Gamma_{t1}: 2 \mu_1 \left[-\frac{1}{7} B_2 + \frac{3}{28} B_4 \right] + \mu_3 \left[\frac{2}{7} B_2 + \frac{2}{7} B_4 \right] \\ & \Gamma_{c5} \rightarrow \Gamma_{t4}: 2 \mu_1 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] + \mu_3 \left[-\frac{2}{7} B_2 + \frac{1}{21} B_4 \right] \\ & \Gamma_{c5} \rightarrow \Gamma_{t5}: 2 \mu_1 \left[-\frac{1}{14} B_2 - \frac{1}{14} B_4 \right] + \mu_3 \left[+\frac{1}{7} B_2 - \frac{4}{21} B_4 \right]. \end{aligned} \right\} \quad (19)$$

For use of the formalism, expressed in eq. 10, the cubic contributions must be written

$$\left. \begin{aligned} & \Gamma_{c3}: E(\text{cub}) = (\mu_1 + \mu_2 + \mu_3) \frac{1}{6} B_4 \\ & \Gamma_{c5}: E(\text{cub}) = -(\mu_1 + \mu_2 + \mu_3) \frac{1}{9} B_4 \end{aligned} \right\} \quad (20)$$

and the tetragonal contributions

$$\left. \begin{aligned} \Gamma_{t3}: E(\text{tetr}) &= \left(\frac{\mu_1 + \mu_2}{2} - \mu_3 \right) \left[\frac{2}{7} B_2 + \frac{5}{42} B_4 \right] \\ \Gamma_{t1}: E(\text{tetr}) &= \left(\frac{\mu_1 + \mu_2}{2} - \mu_3 \right) \left[-\frac{2}{7} B_2 - \frac{5}{42} B_4 \right] \\ \Gamma_{t4}: E(\text{tetr}) &= \left(\frac{\mu_1 + \mu_2}{2} - \mu_3 \right) \left[\frac{2}{7} B_2 - \frac{10}{63} B_4 \right] \\ \Gamma_{t5}: E(\text{tetr}) &= \left(\frac{\mu_1 + \mu_2}{2} - \mu_3 \right) \left[-\frac{1}{7} B_2 + \frac{5}{63} B_4 \right] \end{aligned} \right\} \quad (21)$$

The rhombic contributions of Γ_{t3} and Γ_{t1} together equal 0 and must be considered as interaction effects of the type discussed in the preceding section. The rhombic contribution of Γ_{t4} equals 0, and that of

$$\Gamma_{t5}: E(\text{rhomb}) = \pm (\mu_1 - \mu_2) \left[\frac{3}{14} B_2 - \frac{5}{42} B_4 \right]. \quad (22)$$

It is not possible to use a single parameter E_t for $E(\text{tetr})$ analogous to $(E_1 - E_2) = (\mu_1 + \mu_2 + \mu_3) \frac{5}{18} B_4$ for $E(\text{cub})$. The contributions of B_4 compared with those of B_2 in eq. 21 are $-\frac{4}{3}$ times higher in Γ_{t4} and Γ_{t5} than they are in Γ_{t3} and Γ_{t1} .

The theorem on centres of gravity¹ is valid for all the individual splittings in a given field. However, this theorem is also valid for the further splitting of a degenerate level due to fields of lower symmetry. This is of consequence for the following sections.

Two *d*-Electron Systems.

The energies of the d^2 -levels in tetragonal fields⁵ are compared here with results for d^n -levels in tetragonal fields, analogous to the theory of cubic fields.⁷

We shall first calculate the electron distributions in strong tetragonal fields on the quantum numbers γ_{t5} , γ_{t4} , γ_{t1} , and γ_{t3} in order of increasing energy (in fields with almost no cubic

TABLE 5. d^2 -levels in strong tetragonal fields.

| Degeneracy number | Electron distribution | Levels | Energy | |
|---------------------------|--------------------------|---------------------------|--|---|
| γ_{c3}^2 | 1 | γ_{t3}^2 | ${}^1\Gamma_{t1}$ | $\mu_1 \left[\frac{4}{7} B_2 + \frac{19}{21} B_4 \right] + \mu_3 \left[-\frac{4}{7} B_2 + \frac{2}{21} B_4 \right]$ |
| | 4 | $\gamma_{t3} \gamma_{t1}$ | ${}^1\Gamma_{t3}(c3)$ ${}^3\Gamma_{t3}(c2, {}^3F)$ | $\mu_1 \left[\frac{2}{3} B_4 \right] + \mu_3 \left[\frac{1}{3} B_4 \right]$ |
| | 1 | γ_{t1}^2 | ${}^1\Gamma_{t1}$ | $\mu_1 \left[-\frac{4}{7} B_2 + \frac{3}{7} B_4 \right] + \mu_3 \left[\frac{4}{7} B_2 + \frac{4}{7} B_4 \right]$ |
| $\gamma_{c3} \gamma_{c5}$ | 4 | $\gamma_{t3} \gamma_{t4}$ | ${}^1\Gamma_{t2}(c4, {}^1G)$ ${}^3\Gamma_{t2}(c4)$ | $\mu_1 \left[\frac{4}{7} B_2 + \frac{1}{14} B_4 \right] + \mu_3 \left[-\frac{4}{7} B_2 + \frac{2}{21} B_4 \right]$ |
| | 8 | $\gamma_{t3} \gamma_{t5}$ | ${}^1\Gamma_{t5}$ ${}^3\Gamma_{t5}$ | $\mu_1 \left[\frac{1}{7} B_2 + \frac{13}{42} B_4 \right] + \mu_3 \left[-\frac{1}{7} B_2 - \frac{1}{7} B_4 \right]$ |
| | 4 | $\gamma_{t1} \gamma_{t4}$ | ${}^1\Gamma_{t4}(c5)$ ${}^3\Gamma_{t4}(c5, {}^3F)$ | $\mu_1 \left[-\frac{1}{6} B_4 \right] + \mu_3 \left[\frac{1}{3} B_4 \right]$ |
| | 8 | $\gamma_{t1} \gamma_{t5}$ | ${}^1\Gamma_{t5}$ ${}^3\Gamma_{t5}$ | $\mu_1 \left[-\frac{3}{7} B_2 + \frac{1}{14} B_4 \right] + \mu_3 \left[\frac{3}{7} B_2 + \frac{2}{21} B_4 \right]$ |
| γ_{c5}^2 | 1 | γ_{t4}^2 | ${}^1\Gamma_{t1}$ | $\mu_1 \left[\frac{4}{7} B_2 - \frac{16}{21} B_4 \right] + \mu_3 \left[-\frac{4}{7} B_2 + \frac{2}{21} B_4 \right]$ |
| | 8 | $\gamma_{t4} \gamma_{t5}$ | ${}^1\Gamma_{t5}(c5)$ ${}^3\Gamma_{t5}(c4)$ | $\mu_1 \left[\frac{1}{7} B_2 - \frac{11}{21} B_4 \right] + \mu_3 \left[-\frac{1}{7} B_2 - \frac{3}{21} B_4 \right]$ |
| | 6 | γ_{t5}^2 | ${}^1\Gamma_{t1}$ ${}^1\Gamma_{t3}(c3)$ ${}^1\Gamma_{t4}(c5)$ ${}^3\Gamma_{t2}(c4)$ | $\mu_1 \left[-\frac{2}{7} B_2 - \frac{2}{7} B_4 \right] + \mu_3 \left[\frac{2}{7} B_2 - \frac{8}{21} B_4 \right]$ |

contributions, the order of γ_{t4} and γ_{t1} is inverted). It is fortunate that the corresponding cubic quantum numbers $\gamma_5, \gamma_5, \gamma_3$, and γ_3 are then definitely fixed. Table 2 is used for the vector product $\gamma_{tp} \gamma_{tq}$ when $p \neq q$. This case is not restricted by the Pauli exclusion principle, and thus both values of $S = 1$ and 0 occurs. The case $p = q$ is more difficult. When γ_{tp} has $e = 1$, the electron pair γ_{tp}^2 is a closed shell, the term is $^1F_{t1}$. When $e = 2$, as in γ_{t5}^2 , it is necessary to collect further information. The known case of d^2 -levels gives $S = 1$ for $^3F_{t2}$ and $S = 0$ for the three others $^1F_{t1}$, $^1F_{t3}$, and $^1F_{t4}$. Table 5 give the energies in strong tetragonal fields of these levels, depending on the two parameters $\mu_1 (= \mu_2)$ and μ_3 .

The levels of Table 5 can be divided as follows: In cases where more levels with the same tetragonal quantum number are present in the same of the three groups $\gamma_{c3}^2, \gamma_{c3}\gamma_{c5}$, and γ_{c5}^2 , nothing can be said with certainty in connection with a single level in weak fields. In cases where only one level with the same tetragonal quantum number is present in a group, the cubic quantum number is certain. This can then either be exhibited by one level, which has the given S in the whole d^2 -system, or the cubic number can be exhibited more times. In the γ_{c3}^2 group the former case occurs in $^3F_{t3}$, which can only be the weak field level $^3F(^3F_{c2})$ while the latter case occurs in $^1F_{t3}$, which surely is a $^1F_{c3}$ state, but which cannot be identified with certainty with any atomic term, since 1D and 1G both have $^1F_{c3}$ -levels.

In the best determined class, which contains $^3F_{t3}(^3F)$, $^1F_{t2}(^1G)$, and $^3F_{t4}(^3F)$, the energy (given in Table 5) in strong crystal-fields is verified in ref. 5. The partially determined class is represented e. g. by the two $^3F_{t2}$ -levels:

$$\left. \begin{aligned} ^3F_{t2}(^3F): & \mu_1 \left[-\frac{4}{35} B_2 - \frac{3}{14} B_4 \right] + \mu_3 \left[\frac{4}{35} B_2 - \frac{2}{7} B_4 \right] \\ ^3F_{t2}(^3P): & \mu_1 \left[\frac{2}{5} B_2 \right] + \mu_3 \left[-\frac{2}{5} B_2 \right] \end{aligned} \right\} \quad (23)$$

The former is equal to the energy of $\frac{4}{5} \gamma_{t5}^2 + \frac{1}{5} \gamma_{t3} \gamma_{t4}$, and the latter to $\frac{1}{5} \gamma_{t5}^2 + \frac{4}{5} \gamma_{t3} \gamma_{t5}$. Thus the intermixing coefficients given

in Table 4 seem to apply to the problem of distributing strong tetragonal fields with the intermediate step of strong cubic on the weak tetragonal fields. If it is allowable to use the "centre of gravity"-theorem on the ${}^3T_{e4}$ by beginning tetragonality, it should further be valid that $E(\text{tetr})$ in ${}^3T_{t5}$ in the levels should equal $-\frac{1}{2}E(\text{tetr})$ in the corresponding ${}^3T_{t2}$. Thus

$$\left. \begin{aligned} {}^3T_{t5}({}^3F, c4): & \mu_1 \left[\frac{2}{35} B_2 - \frac{11}{28} B_4 \right] + \mu_3 \left[-\frac{2}{35} B_2 - \frac{3}{28} B_4 \right] \\ {}^3T_{t5}({}^3P, c4): & \mu_1 \left[-\frac{1}{5} B_2 \right] + \mu_3 \left[\frac{1}{5} B_2 \right] \end{aligned} \right\} \quad (24)$$

The latter result in eq. 24 is again confirmed⁵ while the former result is complicated by the fact that two ${}^3T_{t5}$ occur in 3F , and their mutual interaction thus is also reckoned. But the diagonal sum-rule can be applied to all the ${}^3T_{t5}$. Their total energy is to be

$$\left. \begin{aligned} \sum {}^3T_{t5} &= \gamma_{t3} \gamma_{t5} + \gamma_{t1} \gamma_{t5} + \gamma_{t4} \gamma_{t5} \\ &= \mu_1 \left[-\frac{1}{7} B_2 - \frac{1}{7} B_4 \right] + \mu_3 \left[\frac{1}{7} B_2 - \frac{4}{21} B_4 \right] \end{aligned} \right\} \quad (25)$$

and when the energy of ${}^3T_{t5}({}^3P)$ is subtracted,

$$2 {}^3T_{t5}({}^3F) = \mu_1 \left[+\frac{2}{35} B_2 - \frac{1}{7} B_4 \right] + \mu_3 \left[-\frac{2}{35} B_2 - \frac{4}{21} B_4 \right] \quad (26)$$

also found by the direct calculation.⁵

Thus it seems possible by application of the best determined levels and by extended use of the theorem concerning the centres of gravity to determine all or nearly all the energies of tetragonal levels. The restriction (also imposed on the method used in ref. 7) is that only average values of several levels with the same $2S+1T_{tn}$ can be estimated.

Special interest is connected with the ground-state of diamagnetic nickel (II) complexes. Due to Pauli's holeequivalence theorem, it is the level among the 1D -levels (see Fig. 3) which has the highest energy in strong tetragonal fields in d^2 -systems. Previously⁵ it has been discussed, if ${}^1T_{t2}({}^1G, {}^1T_{e4})$ was the ground-state in the rather strong tetragonal field occurring in the square-planar

complexes of stilbenediamine, cyanide, etc. Rather, the state ${}^1T_{11}({}^1D, {}^1G_{c3})$ transferred to the strong tetragonal field state γ_{t3}^2 is lowest, due to second-order effects in the crystal-field strength, while ${}^1T_{12}$ was mentioned as having the lowest energy among the singlet states at more moderate crystal-field strengths.

In cubic complexes, ${}^1G_{c3}({}^1D)$ will at even quite small field strengths have the linear energy expression ($\mu_1 = \mu_2 = \mu_3$)

$$E = \frac{4}{7}({}^1D) + \frac{3}{7}({}^1G) + \mu_1 B_4, \quad (27)$$

while the cubic ground-state ${}^3F_{c2}({}^3F)$ has always

$$E = ({}^3F) + \mu_1 B_4 \quad (28)$$

(see Table 4). The energy differences between the two states are thus nearly constant*, being the differences between terms in the free ion:

$$E({}^1G_{c3}) - E({}^3F_{c2}) = \frac{4}{7}({}^1D) + \frac{3}{7}({}^1G) - ({}^3F). \quad (29)$$

Exceptionally these energies are not known** from atomic spectroscopy,¹² but can with a probable error $\sim 1000 \text{ cm}^{-1}$ be predicted from the theory of CONDON and SHORTLEY¹³ to be $({}^1D) = 13000 \text{ cm}^{-1}$ and $({}^1G) = 22000 \text{ cm}^{-1}$, when $({}^3F) = 0 \text{ cm}^{-1}$. Thus, the energy difference of eq. 29 will be $\sim 17000 \text{ cm}^{-1}$. In $Ni(H_2O)_6^{++}$ measured on the Cary spectrophotometer a very weak band has been found as a shoulder at 18500 cm^{-1} with a half-width 500 cm^{-1} . It may be identified as a ${}^3F_2(F) \rightarrow {}^1G_5(D)$ transition which is predicted $\sim 23000 \text{ cm}^{-1}$, or the similar ${}^1G_3(D)$ predicted $\sim 17000 \text{ cm}^{-1}$.

In tetragonal complexes the energy of ${}^3F({}^3F_{c2})$ has no tetragonal contributions (eq. 10) while $\gamma_{c3}^2({}^1G_{c3})$ will split up, $\gamma_{t3}^2({}^1T_{11})$ being the lowest state. If it is assumed (in analogy with the arguments given for the second class of states in Table 5) that the state in eq. 27 will take over also all the strong field

* Nothing is known about the cause of diamagnetism in bis (triarsine) nickel (II) ion¹⁴ which is the only nickel (II) complex supposed to be cubic and diamagnetic.

** Recently, SHENSTONE¹⁰ has found 1D at 14032 cm^{-1} and 1G at 23109 cm^{-1} . (Added in proof).

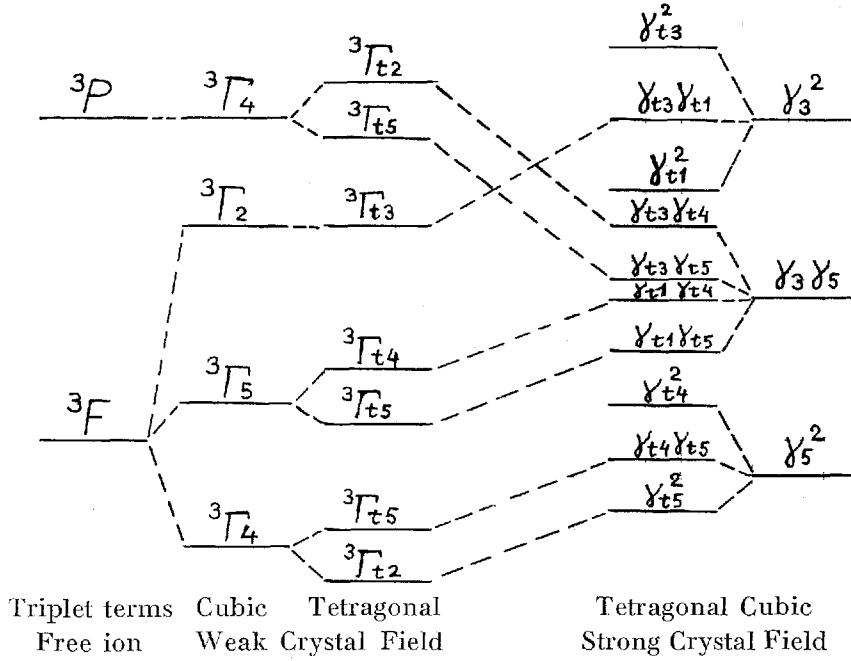


Fig. 2. Triplet states of d^2 in weak and strong crystal fields of cubic and tetragonal symmetry.

tetragonal splitting by being a strong cubic field state, its energy will be ($\mu_1 = \mu_2 > \mu_3$)

$$E = \frac{4}{7}(^1D) + \frac{3}{7}(^1G) + \mu_1 \left[\frac{4}{7}B_2 + \frac{19}{21}B_4 \right] + \mu_3 \left[-\frac{4}{7}B_2 + \frac{2}{21}B_4 \right]. \quad (27)$$

The energy of $^1\Gamma_{t2}$ (1G , $^1\Gamma_{c4}$) is then exactly

$$E = (^1G) + \mu_1 \left[\frac{4}{7}B_2 + \frac{1}{14}B_4 \right] + \mu_3 \left[-\frac{4}{7}B_2 + \frac{2}{21}B_4 \right]. \quad (28)$$

Since the difference between the energy in eq. 27 and 28 is composed of the positive parts $\frac{4}{7}\{(^1G) - (^1D)\} \sim 5000 \text{ cm}^{-1}$ and $\mu_1 \left[-\frac{5}{6}B_4 \right]$ (this is positive due to the hole-formalism⁴ in d^8 -systems) of the order of magnitude $\frac{1}{2}(E_1 - E_2)$ in the corre-

the yellow diamagnetic complexes with their principal band maximum $\sim 22000 \text{ cm}^{-1}$ (with $\text{Ni}(\text{CN})_4^{--}$ on the front with 32000 cm^{-1}) have quite large energy differences between their states, the red ones $\sim 20000 \text{ cm}^{-1}$ are presumably only diamagnetic with some difficulties. E. g. the red nickel (II) inner salt with bis (acetylaceton) ethylenediimine is probably strained by the tendency of the Schiff base-ligand to be planar. The complex, known to be nearest the limit of paramagnetism, is the salmon pink $[\text{Ni en}_2][\text{Ag Br J}]_2$ of NYHOLM¹⁴ (we have also prepared the similar salts with the anions $[\text{Ag Br}_2]^-$ and $[\text{Ag J}_2]^-$ by precipitation with saturated solutions of the silver halide complexes in concentrated solutions of the sodium halides), while the tetra (C, C, C', C') methylsubstituted ethylenediamine¹⁵ forms stable yellow nickel (II) complexes in solution. The absorption spectra of several nickel (II) complexes with these and other amines are now being studied in this laboratory. Fig. 2 and 3 show how the various levels in a d^2 -system are split up by crystal fields of different symmetries. Fig. 2 gives the triplet levels and Fig. 3 the singlet levels.

Three and Four d -Electrons.

As pointed out by SANTEN and WIERINGEN¹⁶ the maximum values of S in d^n -systems give especially regular crystal-field splittings. These are inverted in some cases, viz. for D -states in octahedral complexes:

$$\left. \begin{array}{ll} \text{Regular } (F_5 \text{ lowest}) & \text{Inverted } (F_3 \text{ lowest}) \\ {}^2D(d) & {}^5D(d^4) \\ {}^5D(d^6) & {}^2D(d^9) \end{array} \right\} \quad (30)$$

and for F -states in octahedral complexes:

$$\left. \begin{array}{ll} \text{Regular } (F_4 \text{ lowest}) & \text{Inverted } (F_2 \text{ lowest}) \\ {}^3F(d^2) & {}^4F(d^3) \\ {}^4F(d^7) & {}^3F(d^8) \end{array} \right\} \quad (31)$$

A closer investigation shows that these inversion rules also apply to the tetragonal splitting. Thus the numerical results^{4, 5} for

P -, D -, and F -states of highest multiplicity can easily be adapted to these cases.

Since there will hardly be any possibilities of comparing the theory with experimental data for states of lower S in the magnetically normal complexes, the lengthy calculations along the lines given above will not be performed here. It may be noted that the strong tetragonal field states of $\gamma_{t5}^a \gamma_{t4}^b \gamma_{t1}^c \gamma_{t3}^d$ can be found by direct multiplication from Table 2, when the result of γ_{t5}^2 and the hole-formalism $\gamma_{t5}^3 = \gamma_{t5}$ is remembered. But a point of great chemical interest is the behaviour of the lower states of magnetically anomalous complexes. According to SANTEN and WIERINGEN¹⁶ only d^4 -, d^5 -, d^6 -, and d^7 -systems should give magnetically anomalous complexes of cubic symmetry since they are the only ones which have holes in the γ_5 -shell in the magnetically normal state, to which γ_3 -electrons can be transferred under pairing and decrease in S . This is in very good agreement with experience. The best known diamagnetic complexes of the first transition group are the octahedral cobalt (III) complexes. Their ground-state, ${}^1\Gamma_{c1}(\gamma_5^6)$ is only once degenerate and is thus undisturbed by tetragonal and rhombic effects. Second-order effects can only occur⁷ from $\gamma_5^4 \gamma_3^2$ states, which are so excited that the effects of nondiagonal elements K of eq. 13 are negligible, except at very small $(E_1 - E_2)$, where they repulse γ_5^6 from its high free-ion energy E (intermixed) down along the line in the Orgel diagram¹¹

$$E = E(\text{intermixed}) - \frac{12}{5}(E_1 - E_2). \quad (32)$$

The value of E (intermixed) must mostly be composite of 1G and 1I . The energies of singlet terms in the free cobalt (III) ion will probably never be found by atomic spectroscopy, Racah's theory¹⁷ for the d^n -terms give the expression in Condon-Shortley parameters:¹³

$$\left. \begin{aligned} E({}^1G) &= 6F_0 - 5F_2 - \frac{13}{2}F_4 \\ &\pm \sqrt{708(F_2 - 5F_4)^2 - 420(F_2 - 5F_4)F_4 + 11025F_4^2} \\ E({}^1I) &= 6F_0 - 15F_2 - 9F_4 \\ E({}^5D) &= 6F_0 - 21F_2 - 189F_4. \end{aligned} \right\} \quad (33)$$

With the reasonable¹³ values of $F_2 = 2000 \text{ cm}^{-1}$ and $F_4 = 200 \text{ cm}^{-1}$ the order of magnitude of the energy difference between the lowest singlet state and 5D is found to be 48000 cm^{-1} . Since the lowest cubic state with $S = 2$, viz. $^5T_5 (^5D)$, has the slope $-\frac{2}{5}(E_1 - E_2)$ in the Orgel diagram, it is seen from eq. 32 that $(E_1 - E_2)$ must be at least 24000 cm^{-1} in order to get diamagnetism in cobalt (III). This is already the case in $Co(H_2O)_6^{+++}$ as found in alums by ASMUSSEN.¹⁸

While the first band in chromium (III) complexes gives an almost exact measure of $(E_1 - E_2)$ because⁷ the transition $^3T_2 (^3F, \gamma_5^3) \rightarrow ^3T_5 (^3F, \gamma_5^2 \gamma_3)$ has no intermixing with different values in strong and weak cubic fields, it is not possible to make a similar statement on cobalt (III) complexes. It is only possible to identify the four states of $\gamma_5^5 \gamma_3$ in strong crystal-fields,^{7,11} the two strong bands being due to $S = 0$, 1T_4 and 1T_5 , while the weak band discovered in the red⁶ must be due to either 3T_4 or 3T_5 with $S = 1$. The constant energy difference in the two strong bands $\sim 8000 \text{ cm}^{-1}$ is in our opinion due to intermixing of free ion-terms in the diagonal elements in eq. 13, and it would then be accidental if it was equal to $12 F_2 - 60 F_4$ as maintained by ORGEL.¹¹

The two excited states have the tetragonal splittings $^1T_{c4} \rightarrow ^1T_{t2} + ^1T_{t5}$ and $^1T_{c5} \rightarrow ^1T_{t4} + ^1T'_{t5}$. If it is assumed that these states have no interaction with other states, their $E(\text{tetr})$ (see eq. 10) will be: B_2 and $B_4 > 0$)

$$\left. \begin{aligned} ^1T_{t5} &= \gamma_{t5}^3 \gamma_{t4}^2 \gamma_{t1}: (\mu_1 - \mu_3) \left[-\frac{1}{7} B_2 - \frac{25}{126} B_4 \right] \\ ^1T_{t2} &= \gamma_{t5}^4 \gamma_{t4} \gamma_{t3}: (\mu_1 - \mu_3) \left[\frac{5}{18} B_4 \right] \\ ^1T'_{t5} &= \gamma_{t5}^3 \gamma_{t4}^2 \gamma_{t3}: (\mu_1 - \mu_3) \left[\frac{3}{7} B_2 + \frac{5}{126} B_4 \right] \\ ^1T_{t4} &= \gamma_{t5}^4 \gamma_{t4} \gamma_{t1}: (\mu_1 - \mu_3) \left[-\frac{4}{7} B_2 + \frac{5}{126} B_4 \right] \end{aligned} \right\} \quad (34)$$

The assumption of no interaction between the states will probably not be valid in the case of $^1T_{t5}$ and $^1T'_{t5}$. ORGEL¹¹ is of course

right in maintaining that Γ_{c5} has no first-order tetragonal splitting in contrast to Γ_{c4} . But this situation may be reversed in strong crystal fields. Of the energies in eq. 34 it may be concluded that ${}^1\Gamma_{t2}$ has so small a value of E (tetr) (without B_2 contributions) that if the theorem of centre of gravity can be applied to this and the other level of ${}^1\Gamma_{c4}$, it has a very small tetragonal splitting as compared with the ${}^1\Gamma_{t4}$ plus a mixture of ${}^1\Gamma_{t5}$ and ${}^1\Gamma'_{t5}$, leading to ${}^1\Gamma_{c5}$.

It is empirically well known¹⁹ that the first of the two strong cobalt (III) bands generally show much larger tetragonal splittings than the other. As seen above, it can be interpreted by use of eq. 34 as being the transition to ${}^1\Gamma_{c5}$ contrary to ${}^1\Gamma_{c4}$. In pronounced tetragonal fields, as found in trans- $[\text{Co en}_2\text{Cl}_2]^+$, the lowest excited state is then ${}^1\Gamma_{t4} (\gamma_{t5}^4 \gamma_{t4} \gamma_{t1})$. At a tetragonality so strong that γ_{t4} and γ_{t1} has the same energy (as found e. g. in copper (II) complexes) this state should be competing with ${}^1\Gamma_{c1} (\gamma_{t5}^4 \gamma_{t4}^2)$ as ground-state.

The question of tetragonal splittings in chromium (III) complexes seems quite complicated. Not only does the first strong band show this splitting,¹¹ but as will be shown in another publication by one of us, the second band is strongly split in the bluish grey hydroxo form of the chromium (III) ethylenediaminetetraacetate.²⁰ C. E. SCHÄFFER of this laboratory has discovered that the dinuclear "basic rhodo" complex,²¹ which is formed transiently by air-oxidation of chromium (II) in ammonia water, shows on the Cary spectrophotometer four very narrow bands in the near ultraviolet. The first band ${}^3\Gamma_{c2} \rightarrow {}^3\Gamma_{c5}$ should show little first-order tetragonal splitting, since one of the levels in ${}^3\Gamma_{c5}$ is ${}^3\Gamma_{t4} (\gamma_{t5}^2 \gamma_{t8})$, which has the B_2 -contribution = 0.

Some of the strong bands in magnetically normal complexes predicted by the crystal field theory are not very easily detected. The most prominent examples are:

$$\left. \begin{aligned} d^2: {}^3\Gamma_4 ({}^3F) &\rightarrow {}^3\Gamma_2 ({}^3F) \\ d^3: {}^3\Gamma_2 ({}^3F) &\rightarrow {}^3\Gamma_4 ({}^3P) \\ d^7: {}^3\Gamma_4 ({}^3F) &\rightarrow {}^3\Gamma_2 ({}^3F). \end{aligned} \right\} \quad (35)$$

In d^2 and d^7 the excited states are only once degenerate on a $(2L + 1)$ basis and might be suspected to give weaker bands

than the other, three-fold degenerate states with maximum S . In vanadium (III), the band seems nevertheless observed at 38000 cm^{-1} in the reflection spectrum of $K_2[VF_5H_2O]$ as measured on the Beckman DU. From the other bands in this complex a wave-number 35000 cm^{-1} is predicted. In cobalt (II) the band is now identified with the quite weak band⁶ at 16000 cm^{-1} in $Co(H_2O)_6^{++}$ and the somewhat stronger bands in $Co(NH_3)_6^{++}$ at 18200 cm^{-1} and in $Coen_3^{++}$ at 18500 cm^{-1} as described in the ninth paper of this series.²² Since the band in purely cubic complexes corresponds to the energy $\frac{9}{5}(E_1 - E_2)$, this quantity is now assumed to be 9000 cm^{-1} in the aquo ion, which must be slightly rhombic, as seen above.

d^3 is represented in vanadium (II) and chromium (III). In solutions of vanadium in 6 M HCl , reduced by zinc, a third band can be observed at 26500 cm^{-1} besides the two at 12200 and 18000 cm^{-1} . Since it does not have the place of the second band of vanadium (III), it is most probably one of the bands given in eqs. 35. Since $(E_1 - E_2)$ is as small as 12000 cm^{-1} , the bands are distributed nearly as in $Nien_3^{++}$: the two F_4 have nearly their minimum distance⁷ $= 2K$ in eq. 13. In chromium (III), low band at 38000 cm^{-1} observed of TSUCHIDA²³ in $Cr(H_2O)_6^{+++}$ may represent the third strong band with the corresponding $(E_1 - E_2) = 17500\text{ cm}^{-1}$. The red solutions of chromium (III) chloride in absolute ethanol saturated with lithium chloride (probably containing $CrCl_3 \cdot 6LiCl$) show also the third band clearly. Here the two first bands are shifted much toward the red, 12000 and 19000 cm^{-1} , respectively, while a similar band is observed at 26000 cm^{-1} . Further out in the ultraviolet, the electron transfer spectrum due to the easy remove of electrons from chloride ions are observed.

Five d -Electrons.

These systems⁷ have no first-order crystal-field splittings in complexes of cubic symmetry. Their second-order interactions can be treated by methods given above in the second section. The absorption spectra of magnetically normal manganese (II) and iron (III) consist of very weak bands⁷ due to the transitions

from the ground-state 6S to splittings of quartet states. Besides this, iron (III) compounds have very intense electron transfer spectra as seen in $Fe(OH)^{++}$, $Fe(SCN)_3$, $FeS_2O_3^+$, etc.

Among the quartet states, 4F_1 and 4F_2 are only represented once, and they have both $N = 2$ in eq. 12, as also ${}^6F_1({}^6S)$. 4F_3 is represented twice with $N = 2$ (4D and 4G). They continue also without interaction in strong crystal-fields. Probably the two 4G -levels 4F_3 and 4F_1 are represented in bands⁶ at 24900 and 25150 cm^{-1} . These narrow bands were also found by GIELESSEN²⁴ and in solid manganese (II) salts they split into 12 components. Due to the Kramer degeneracy, more than 6 were not expected, even due to (L, S) coupling effects. But many of the narrow bands found by GIELESSEN are probably coupled with vibrations. Of great importance for the observed spectra are the states 4F_4 , which occur in 4P , 4F , and 4G . They have the energies in the free manganese (II) ion¹² 29200, 43600, and 26800 cm^{-1} respectively. The two terms 4G and 4P are liable to interact strongly due to the small distance of the terms. If in the strong crystal field the lowest level has the energy in cubic complexes

$$Mn(II) {}^4F_4(\gamma_5^4 \gamma_3): 28000 \text{ cm}^{-1} - (E_1 - E_2). \quad (36)$$

$(E_1 - E_2)$ is then = 9200 cm^{-1} in $Mn(H_2O)_6^{++}$, which seems very probable, and similar calculations for $Fe(H_2O)_6^{+++}$ give $(E_1 - E_2) = 22000 \text{ cm}^{-1}$. The middle 4F_4 in $Mn(H_2O)_6^{++}$ should be placed $\sim 30000 \text{ cm}^{-1}$ and is probably the band⁶ at 29700 cm^{-1} . 4F_5 is finally the explanation of the bands at 23000 cm^{-1} in manganese (II) and at 18500 cm^{-1} in iron (III).⁶ The three interacting levels are here due to 4D , 4F , and 4G .

Geometrical Configuration and Absorption Spectrum.

Due to the fact that only three parameters μ_1 , μ_2 , and μ_3 determine the spectrum of a given complex with constant⁴ R , Z and electron configuration, the symmetry of the crystal fields is often surprising high. Table 6 gives the symmetry of complexes with at most three different ligands A , B , C in the octahedral complexes $MA_aB_bC_c$ ($a \geq b \geq c$) with six equal distances.

TABLE 6. Symmetry of octahedral complexes with at most three different ligands A , B and C .

| | | | | | |
|------------------------|-----|------------------------|-----|----------------------------|-----|
| MA_6B | c | (1, 2, 6) MA_3B_3 | r | (B 1,6 C 2) MA_3B_2C | r |
| MA_5B | t | cis (1, 2) MA_4BC | r | (B 1,2 C 3,4) $MA_2B_2C_2$ | r |
| cis (1, 2) MA_4B_2 | t | trans (1, 6) MA_4BC | t | (B 1,2 C 3,5) $MA_2B_2C_2$ | t |
| trans (1, 6) MA_4B_2 | t | (B 1,2 C 3) MA_3B_2C | t | (B 1,6 C 2,3) $MA_2B_2C_2$ | t |
| (1, 2, 3) MA_3B_3 | c | (B 1,2 C 4) MA_3B_2C | r | (B 1,6 C 2,4) $MA_2B_2C_2$ | r |

Among the tetragonal complexes, the tetragonality can be measured by $(\mu_1 - \mu_3)$ as seen from eq. 21 and as also found directly from ref. 4. It is seen that this quantity is (-2) times as small in cis MA_4B_2 as in trans MA_4B_2 , since

$$\left. \begin{array}{ll} \text{cis-}MA_4B_2 & \text{trans-}MA_4B_2 \\ \mu_1 = \mu_2 = \mu_A + \mu_B & \mu_1 = \mu_2 = 2 \mu_A \\ \mu_3 = 2 \mu_A & \mu_3 = 2 \mu_B \\ \mu_1 - \mu_3 = \mu_B - \mu_A & \mu_1 - \mu_3 = 2 \mu_A - 2 \mu_B \end{array} \right\} (37)$$

This is the explanation of the tetragonal splitting being much more distinct¹⁹ in trans-complexes, while it only gives broadening of the bands in the cis-complexes. Here the splitting is (-1) time the splitting of mono-substituted complexes MA_5B , which have $\mu_1 - \mu_3 = \mu_A - \mu_B$, i. e. the splitting is inverted.

In applying these rules to observed spectra it is necessary to consider several facts. First, chelate ligands are treated as composed of the individual coordinating links. Especially symmetrical chelates such as ethylenediamine or oxalate have AA function. Secondly, when the pure MA_6 and MB_6 complexes have nearly the same spectra, the mixed complexes MA_nB_{6-n} will show very small changes (formally, because $\mu_B - \mu_A \sim 0$). These cases can be found from the spectrochemical series first developed by FAJANS²⁵ and later extended by TSUCHIDA²³:

$$\left. \begin{array}{l} J^- < Br^- < Cl^- \lesssim OH^- < RCOO^- < NO_3^- < F^- \lesssim H_2O \\ < SCN^- < NH_3 < en \lesssim NO_2^- < o\text{-}phen \lesssim dip < CN^- \end{array} \right\} (38)$$

The anions find quite fixed positions between the neutral molecules in this series. Thirdly, the effects of making a purely cubic complex MA_6 less symmetrical by substitution to MA_5B , MA_4B_2 . . .

are different, according to the ground-state being only once degenerate in cubic symmetry (as in chromium (III), nickel (II), diamagnetic cobalt (III) complexes, etc.) or it is several times degenerate (as in titanium (III), cobalt (II), copper (II), etc.). In the former cases the tetragonal splitting of a band does not move its centre of gravity determined by the cubic contribution $\mu_1 + \mu_2 + \mu_3$, while the latter cases have a predominant hypsochromic influence of unsymmetrical substitution, because the ground-state is decreased in energy also by tetragonal fields. Generally spoken, the latter type of complex with several times degenerate ground-state in cubic symmetry can show phenomena such as the "pentammine effect" in copper (II) complexes.⁴ They have a tendency towards showing characteristic coordination numbers 2 and 4 in the sense of J. BJERRUM²⁶, while the non-degenerate cubic ground-states give nearly constant consecutive equilibrium constants, corrected for statistical effects and steric interaction between the ligands.

The non-degenerate, purely cubic type is very promising for calculation of spectra of poly-nuclear species, so abundant in chromium (III) and cobalt (III) chemistry. C. E. SCHÄFFER will elsewhere publish absorption spectra of these compounds. E. g. the brown cation²⁷ $[Co \{(OH)_2 Co (NH_3)_4\}_3]^{+6}$ has exactly the spectrum predicted of a mixture of the mono-nuclear links, one part of the hypothetical $[Co (OH)_6]^{-3}$ (determined from eq. 38) and three parts of $cis [Co (NH_3)_4 (OH)_2]^+$, with the strong electron transfer spectrum from $OH^- + Co^{+3} \rightarrow OH + Co^{+2}$ superposed in the near ultraviolet.

***d*-Electrons in Crystal Fields of Trigonal Symmetry.**

The trigonal symmetry D_3 is characterized by the three 3-dimensional vectors ($E, 2 C_3, 3 C_2'$)²⁸:

$$\left. \begin{aligned} C(\Gamma_{A1}) &= (1, 1, 1) \\ C(\Gamma_{A2}) &= (1, 1, -1) \\ C(\Gamma_{A3}) &= (2, -1, 0). \end{aligned} \right\} \quad (39)$$

For different values of L , the possible quantum numbers are:

$$\left. \begin{aligned}
 C(S) &= (1, 1, 1) = C(\Gamma_{A1}) \\
 C(P) &= (3, 0, -1) = C(\Gamma_{A2}) + C(\Gamma_{A3}) \\
 C(D) &= (5, -1, 1) = C(\Gamma_{A1}) + 2C(\Gamma_{A3}) \\
 C(F) &= (7, 1, -1) = C(\Gamma_{A1}) + 2C(\Gamma_{A2}) + 2C(\Gamma_{A3}) \\
 C(G) &= (9, 0, 1) = 2C(\Gamma_{A1}) + C(\Gamma_{A2}) + 3C(\Gamma_{A3}) \\
 C(H) &= (11, -1, -1) = C(\Gamma_{A1}) + 2C(\Gamma_{A2}) + 4C(\Gamma_{A3}) \\
 C(I) &= (13, 1, 1) = 3C(\Gamma_{A1}) + 2C(\Gamma_{A2}) + 4C(\Gamma_{A3}),
 \end{aligned} \right\} \quad (40)$$

The multiplication table is:

$$\left. \begin{array}{c|ccc}
 & \Gamma_{A1} & \Gamma_{A2} & \Gamma_{A3} \\
 \hline
 \Gamma_{A1} & \Gamma_{A1} & \Gamma_{A2} & \Gamma_{A3} \\
 \Gamma_{A2} & \Gamma_{A2} & \Gamma_{A1} & \Gamma_{A3} \\
 \Gamma_{A3} & \Gamma_{A3} & \Gamma_{A3} & \Gamma_{A1} + \Gamma_{A2} + \Gamma_{A3}
 \end{array} \right\} \quad (41)$$

The crystal field of a trigonal bipyramid has this symmetry. If one of the three equal dipoles in the planar triangle is denoted by μ_1 , and one of the two equal dipoles in the perpendicular axis through the centre of the triangle by μ_2 , the energy of the three possible states of one d -electron is:

$$\left. \begin{aligned}
 E(\gamma'_{A3}) &= \mu_1 \left[\frac{3}{7} B_2 + \frac{3}{56} B_4 \right] + \mu_2 \left[-\frac{4}{7} B_2 + \frac{2}{21} B_4 \right] \\
 E(\gamma_{A3}) &= \mu_1 \left[-\frac{3}{14} B_2 - \frac{3}{14} B_4 \right] + \mu_2 \left[+\frac{2}{7} B_2 - \frac{8}{21} B_4 \right] \\
 E(\gamma_{A1}) &= \mu_1 \left[-\frac{3}{7} B_2 + \frac{9}{28} B_4 \right] + \mu_2 \left[+\frac{4}{7} B_2 + \frac{4}{7} B_4 \right].
 \end{aligned} \right\} \quad (42)$$

It is seen that the relative position of these energy levels are highly dependent on the ratio B_2/B_4 and μ_1/μ_2 . For the limiting case $\mu_1 = 0$, the three energies are equal to the similar limits in the tetragonal case for γ_{t3} ($= \gamma_{t4}$), γ_{t5} , and γ_{t1} , respectively.

For the special case $\mu_1 = \frac{4}{3}\mu_2$, the B_2 contributions vanish:

$$\left. \begin{aligned} E(\gamma'_{\Delta 3}) &= \mu_2 \left[\frac{1}{6} B_4 \right] \\ E(\gamma_{\Delta 3}) &= \mu_2 \left[-\frac{2}{3} B_4 \right] \\ E(\gamma_{\Delta 1}) &= \mu_2 [B_4]. \end{aligned} \right\} \quad (43)$$

Just as in the cubic symmetry, the sum of dipole moments in the plane is twice as large as the sum of dipole moments along the perpendicular axis in this particular case. While the other types of crystal field symmetry, treated in this paper, are represented in octahedral complexes, the trigonal symmetry corresponds to only five-coordinated complexes. These are of special interest as a probable intermediate configuration occurring in exchange reactions by dissociation of octahedral complexes involving S_{N1} mechanisms.²⁹

Summary.

The group-theoretical derivation of the possible states in crystal fields of cubic, tetragonal, and rhombic symmetry is presented as operations with simple five-dimensional vectors. The problem of interaction between two states alone by going from weak to strong crystal fields is solved. The behaviour of one d -electron in the fields of different symmetry is discussed. The earlier calculations on d^2 -systems are used for comparison with the strong and weak tetragonal fields. The ground-state of diamagnetic nickel (II) complexes is found. In d^3 - and d^4 -systems, the splitting of states with maximum S is inverted, as compared with the corresponding d^2 - and d^1 -states. The magnetically anomalous complexes of these configurations are discussed, and peculiarities in the tetragonal splitting pointed out. Cubic states of d^5 with $S = \frac{3}{2}$ are in some cases strongly interacting. Finally the relative magnitude of the tetragonal splitting in complexes with different distribution of ligands on the six octahedral places is found. Distinction is made between complexes with only once degenerate ground-state in cubic symmetry (which show more regular evolution of spectra and equilibrium constants with

increasing number of a new ligand) as compared with complexes where this is not the case. These latter, which according to VAN VLECK cannot at all be stable in purely cubic symmetry, show higher wave-numbers of the mixed complexes as compared with the limiting complexes MA_6 and MB_6 .

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