SPLITTING OF d^n- TERMS OF TETRAGONAL COMPLEXES IN STRONG FIELDS

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The d-electrons of the central ion play an important role at the development of the properties of complex compounds. In this paper, all the strong field configurations arising from d^n-configurations ($n=1,\ldots 10$) in the complex field of D_{4h} symmetry have been calculated. The irreducible representations and the multiplicity of the splitting products of these terms have been established.

§ 1. *Introduction*

BETHE [1] investigated the splitting of terms of ions in crystals for the first time. He founded the „crystal field method" in 1929 which is also applicable for the theoretical treatment of complex ions. SCHLAPP and PENNEY [2] have used this theory for the calculation of magnetic susceptibilities of crystals containing paramagnetic ions, while FINKELSTEIN and VAN VLECK [3] employed it for the interpretation of the spectrum of chrome alaun in crystalline state. On applying BETHE's crystal field method for electrostatic complexes it is usual to start from the model outlined below. According to the basic assumption of the method the complex ion consists of a central ion being surrounded by the coordination zone. The central ion is a core surrounded by d-electrons while the coordination zone is a point charge system or point dipole system having a well-defined geometric shape.

In the approximation suitable for the model one usually considers the interactions among the individual parts. These are as follows: (i) the interaction of the outer electrons of the central ion and (ii) the influence of the coordination zone (complex field) on the outer electrons of the central ion. These interactions can be conceived as representing perturbations. In such calculations the final aim is to determine the wave functions and energy

levels of the electrons considered. According to the relative size of the interactions considered[1] one can take steps in two different manners.

1. *Weak field case.* When the influence of the complex field on the outer electrons of the central ion is less than the interaction of these electrons among themselves; there exists a weak field. In such a case, in the first approximation disregarding the influence of the complex field only the interactions of the electrons will be taken into account. Thus, in this approximation, the model is reduced to the problem of the spectroscopic gaseous ion. Then the corresponding RUSSEL—SAUNDERS terms are obtained as energies. In the second approximation, due to the perturbation caused by the complex field, the RUSSEL—SAUNDERS terms split.

2. *Strong field case.* Whenever the influence of the complex field is greater than the mutual interaction of the outer electrons of the central ion; there exists a strong field. As then the complex field is strong the state of the outer electrons of the central ion is modified already before affecting the mutual interaction of the electrons. Hence the strong complex field completely or partly removes the degeneracy of the terms. The mutual interactions of the outer electrons must be investigated taking into account the splitting mentioned above. The configurations obtained in this manner split in the complex field.

ILSE and HARTMANN [4] were in 1951 the first to apply for complex ions the weak field approximation of BETHE's theory. Since this time many authors [5] have dealt with similar problems.

For the interpretation of spectra of transition metal complexes the strong field approximation was applied by ORGEL [6]. Subsequently TANABE and SUGANO [7] and ORGEL [8] have elaborated the theory for octahedral complexes of d^n configurations completely. JØRGENSEN [9] has supplied the size of the splittings of all the d^n-terms in strong fields of O_h symmetry. KISS [10] was one of the first who applied these results for the interpretation of spectra. Since then they are used by numerous other authors for the interpretation of spectroscopic [11], [15] and magnetic [12] phenomena.

In most cases O_h symmetry has been assumed, though this means the extreme simplification of the problem considered. Actually, however, a lower symmetry exists. Sometimes already at the beginning the symmetry is not cubic [3], [6], [13], in other cases owing to the JAHN—TELLER effect distortion takes place. Thus *e. g.* JØRGENSEN [14] has stated that a complex of d^4 and d^9 configurations having six identical ligands with cubic symmetry cannot be stable and therefore the cubic symmetry distorts to tetragonal and in the case of d^1 configuration to rhombic. Considering that the complex compounds which are in the centre of spectroscopic interest have lower symmetries than

[1] At this point we have to draw attention to the circumstance that we ought still to examine how, owing to the effect of the complex field, the core changes and how this modified core influences the state of the outer electrons. With regard to these problems which appear only in the course of numerical calculations and even then cause changes only in the radial part of the wave functions of the electrons considered, nevertheless, we ought only to deal with these problems if we want to calculate the integrals occurring in the course of the calculation explicitly.

O_h, it seems to be necessary to determine the splittings caused by strong fields of lower symmetries. Such calculations were hitherto only carried out for the case of D_{4h} symmetry [15], however, only the splittings of some strong field configurations for d^6 electron configuration were determined. Under these circumstances it seems necessary to extend these examinations to the other important cases. Therefore, in this paper, to investigate the splitting of d^n configurations ($n=1, 2, \ldots 10$) in complex fields having D_{4h} symmetry the strong field approximation will be applied.

§ 2. *The classification of energy terms corresponding to the symmetry properties of the complex*

It is known that there exist five d wave functions independent linearly of one another, the linear combinations of which belonging to each irreducible representation of the point group D_{4h} will be determined. Accordingly, the five-dimensional space of the d-functions breaks up into sub-spaces being invariant under the operations of the D_{4h} group. Let us designate with Γ_d the representation of the D_{4h} group which is valid in the five-dimensional reducible space, it will be broken up into irreducible representations as follows:

$$\Gamma_d = A_{1g} + B_{1g} + B_{2g} + E_g. \tag{1}$$

In Table I the character system of D_{4h} group is given. In this, the irreducible representations are denoted as usual (*e. g.* [16]).

In the case of a complex field having D_{4h} symmetry one d-electron, in accordance with (1), can stay in four different states. According to the PAULI exclusion principle, two electrons can stay in the states represented by wave functions[2] denoted by a_{1g}, b_{1g} and b_{2g} and four electrons can stay in e_g.

In the case of d^n configurations, apart from the case $n=1$, a many-electron problem has to be dealt with. Thus, to consider the interactions of d-electrons we have to start from many-electron wave functions which can be represented in the usual way as products of one-electron functions. In making these products, of course, the PAULI principle is to be considered and corresponding with the strong field approximation not the original d-functions but the functions suitable for (1) are used. In this manner, the possible configurations of the strong field (strong field configurations) can be obtained. The spaces of the functions belonging to each configuration of the strong field are generally reducible. Since the d-functions contain the coordinates on even power, the reducible spaces can have irreducible components (splitting products or sub-levels) of g type only. The same holds for spaces spanned by linear combinations or products of functions of d-type, respectively. These reducible spaces are to be reduced according to D_{4h}.

In the first place, the number of the functions belonging to each configuration, *i. e.* the total sum of degeneracy numbers should be determined.

[2] In the following the wave function belonging to a Γ representation will be correspondingly denoted by γ and this γ will be called the function of Γ or γ function as well.

In a state belonging to a j-dimensional irreducible representation $2j$ electrons can stay. If the number of the filled states is k the total sum of degeneracy numbers is given by the formula

$$\frac{(2j)!}{(2j-k)!\cdot k!}. \tag{2}$$

Whenever wave functions of different irreducible representations take part in a given configuration the total sum of the degeneracy numbers is the product of the degeneracy numbers of the states belonging to each configuration. The dimension of the space of the functions belonging to each configuration corresponds to the total sum of degeneracy numbers of the configuration involved. If one knows the total sum of the degeneracy numbers the number and the multiplicity of states belonging to a given configuration may be calculated. To determine the irreducible representations to which these states belong the reduction mentioned above must be carried out in the space of the configurations. To accomplish this the trace system of the representations attained in the reducible space is required. If there is a con-

Table I

D_{4h}	E	C_2	$2C_4$	$2C_2'$	$2C_2''$	i	iC_2	$2iC_4$	$2iC_2'$	$2iC_2''$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
B_{1g}	1	1	−1	1	−1	1	1	−1	1	−1
B_{1u}	1	1	−1	1	−1	−1	−1	1	−1	1
B_{2g}	1	1	−1	−1	1	1	1	−1	−1	1
B_{2u}	1	1	−1	−1	1	−1	−1	1	1	−1
E_g	2	−2	0	0	0	2	−2	0	0	0
E_u	2	−2	0	0	0	−2	2	0	0	0
$(e_g)^2$	6	6	2	−2	−2	6	6	2	−2	−2

figuration which comprises only the functions of one-dimensional irreducible representations the traces wanted are given by a product. The factors of this product are the square or the double of the characters if the filling number is 2 or 1, respectively. If, in turn, there are configurations comprising wave functions of multi-dimensional irreducible representations too the question is much more complicated. There appear configurations containing (e_g) and $(e_g)^3$; their traces are equal, on the other hand, as the degeneracy number of the state e_g is 4 the corresponding traces are the double of the characters of representation E_g. Similarly there occur configurations containing $(e_g)^2$ too. In order to determine the traces of the representation belonging to these

configurations antisymmetrized functions of type $(e_g)^2$ should be formed. Since $j=2$, $k=2$, according to (2) the number of the functions is 6. The traces of the representation obtained in the space of these six functions may be got by studying the behaviour of these functions under the symmetry operations of the D_{4h} group (Table I, last row).

The reductions can be performed by means of traces obtained by the above consideration. If these reductions are known, in most cases it can directly be established to which irreducible representations the already counted terms arising from the splitting belong and their multiplicities may also be calculated. In cases, when a configuration breaks up into functions of irreducible representations of various kinds in the above procedure there remains uncertainty. Under these circumstances, BETHE's method is used for establishing the multiplicities. The essence of this method is that the configurations containing the functions of multi-dimensional irreducible representations split into configurations composed of functions of pure one-dimensional representations by diminishing the symmetry. The multiplicity is given directly. In addition the irreducible representation of the group of lower symmetry, to which the state of multiplicity already known belongs, can be determined. One or two irreducible representations correspond to this representation in D_{4h} symmetry. Nevertheless, this method was also unsuccessful. For this reason BETHE's method has been developped by diminishing the symmetry in several different ways. Then the alternatives obtained in different manners were compared. However, we succeeded in obtaining perfect results by making use of the above reduction.

BETHE's procedure outlined previously can be meglected on applying the following — though rather lengthy, but far more direct — considerations. After determining the terms arising from the reduction new functions which span the subspaces invariant under the symmetry operations of D_{4h} group in the space of the configuration should be formed. If these new functions are known the multiplicities wanted are afforded directly.

§ 3. *Summary of results*

In the manner described in § 2 the terms[3] arising from the splitting of the configurations d^1—d^{10} have been determined. The splitting products are the same in configurations d^n and d^{10-n}. The splitting of the configurations d^1 and d^9, respectively, is given by (1). The d^{10} configuration $[(e_g)^4 (a_{1g})^2 (b_{1g})^2 (b_{2g})^2]$ consists of a single term $^1A_{1g}$. The other results are listed in Tables II, III, IV and V. The division of the Tables is as follows. In the first column, one can find the possible strong field configurations of the d^n electron configurations. In the second one, the total sum of degeneracy numbers of each configuration is denoted. In the third, the number of the splitting products grouped according to their irreducible representations and their multiplicities are given. In the last column, the strong field configurations of

[3] Hereafter referred as to "splitting products" or "sub-levels".

Table II*

d^2	Total sum of $d.n.$	A_{1g}		A_{2g}		B_{1g}		B_{2g}		E_g		d^8
		1	3	1	3	1	3	1	3	1	3	
$(e_g)^2$	6	1			1	1		1				$(a_{1g})^2\,(b_{1g})^2\,(b_{2g})^2\,(e_g)^2$
$(a_{1g})^2$	1	1										$(b_{1g})^2\,(b_{2g})^2\,(e_g)^4$
$(b_{1g})^2$	1	1										$(a_{1g})^2\,(b_{2g})^2\,(e_g)^4$
$(b_{2g})^2$	1	1										$(a_{1g})^2\,(b_{1g})^2\,(e_g)^4$
$(a_{1g})\,(b_{1g})$	4					1	1					$(a_{1g})\,(b_{1g})\,(b_{2g})^2\,(e_g)^4$
$(a_{1g})\,(b_{2g})$	4							1	1			$(a_{1g})\,(b_{1g})^2\,(b_{2g})\,(e_g)^4$
$(b_{1g})\,(b_{2g})$	4			1	1							$(a_{1g})^2\,(b_{1g})\,(b_{2g})\,(e_g)^4$
$(a_{1g})\,(e_g)$	8									1	1	$(a_{1g})\,(b_{1g})^2\,(b_{2g})^2\,(e_g)^3$
$(b_{1g})\,(e_g)$	8									1	1	$(a_{1g})^2\,(b_{1g})\,(b_{2g})^2\,(e_g)^3$
$(b_{2g})\,(e_g)$	8									1	1	$(a_{1g})^2\,(b_{1g})^2\,(b_{2g})\,(e_g)^3$

Table III**

d^3	Total sum of $d.n.$	A_{1g}		A_{2g}		B_{1g}		B_{2g}		E_g		d^7
		2	4	2	4	2	4	2	4	2	4	
$(e_g)^3$	4									1		$(a_{1g})^2\,(b_{1g})^2\,(b_{-g})^2\,(e_g)$
$(a_{1g})^2\,(b_{1g})$	2					1						$(b_{1g})\,(b_{2g})^2\,(e_g)^4$
$(a_{1g})^2\,(b_{2g})$	2							1				$(b_{1g})^2\,(b_{2g})\,(e_g)^4$
$(b_{1g})^2\,(a_{1g})$	2	1										$(a_{1g})\,(b_{2g})^2\,(e_g)^4$
$(b_{1g})^2\,(b_{2g})$	2							1				$(a_{1g})^2\,(b_{2g})\,(e_g)^4$
$(b_{2g})^2\,(a_{1g})$	2	1										$(a_{1g})\,(b_{1g})^2\,(e_g)^4$
$(b_{2g})^2\,(b_{1g})$	2					1						$(a_{1g})^2\,(b_{1g})\,(e_g)^4$
$(a_{1g})^2\,(e_g)$	4									1		$(b_{1g})^2\,(b_{2g})^2\,(e_g)^3$
$(b_{1g})^2\,(e_g)$	4									1		$(a_{1g})^2\,(b_{2g})^2\,(e_g)^3$
$(b_{2g})^2\,(e_g)$	4									1		$(a_{1g})^2\,(b_{1g})^2\,(e_g)^3$
$(e_g)^2\,(a_{1g})$	12	1		1	1	1		1				$(a_{1g})\,(b_{1g})^2\,(b_{2g})^2\,(e_g)^2$
$(e_g)^2\,(b_{1g})$	12	1		1		1		1	1			$(a_{1g})^2\,(b_{1g})\,(b_{2g})^2\,(e_g)^2$
$(e_g)^2\,(b_{2g})$	12	1		1		1	1	1				$(a_{1g})^2\,(b_{1g})^2\,(b_{2g})\,(e_g)^2$
$(a_{1g})(b_{1g})\,(b_{2g})$	8			2	1							$(a_{1g})\,(b_{1g})\,(b_{2g})\,(e_g)^4$
$(e_g)\,(a_{1g})\,(b_{1g})$	16									2	1	$(a_{1g})\,(b_{1g})\,(b_{2g})^2\,(e_g)^3$
$(e_g)\,(a_{1g})\,(b_{2g})$	16									2	1	$(a_{1g})\,(b_{1g})^2\,(b_{2g})\,(e_g)^3$
$(e_g)\,(b_{1g})\,(b_{2g})$	16									2	1	$(a_{1g})^2\,(b_{1g})\,(b_{2g})\,(e_g)^3$

* In the third column the numbers 1 and 3 mean the multiplicities of the terms.
** In the third column the numbers 2 and 4 mean the multiplicities of the terms.

Table IV*

d^4	Total sum of $d.n.$	A_{1g}			A_{2g}			B_{1g}			B_{2g}			E_g			d^6
		1	3	5	1	3	5	1	3	5	1	3	5	1	3	5	
$(e_g)^4$	1	1															$(a_{1g})^2\,(b_{1g})^2\,(b_{2g})^2$
$(e_g)^3\,(a_{1g})$	8													1	1		$(e_g)\,(a_{1g})\,(b_{1g})^2\,(b_{2g})^2$
$(e_g)^3\,(b_{1g})$	8													1	1		$(e_g)\,(a_{1g})^2\,(b_{1g})\,(b_{2g})^2$
$(e_g)^3\,(b_{2g})$	8													1	1		$(e_g)\,(a_{1g})^2\,(b_{1g})^2\,(b_{2g})$
$(a_{1g})^2\,(b_{1g})^2$	1	1															$(e_g)^4\,(b_{2g})^2$
$(a_{1g})^2\,(b_{2g})^2$	1	1															$(e_g)^4\,(b_{1g})^2$
$(b_{1g})^2\,(b_{2g})^2$	1	1															$(e_g)^4\,(a_{1g})^2$
$(e_g)^2\,(a_{1g})^2$	6	1			1			1			1						$(e_g)^2\,(b_{1g})^2\,(b_{2g})^2$
$(e_g)^2\,(b_{1g})^2$	6	1			1			1			1						$(e_g)^2\,(a_{1g})^2\,(b_{2g})^2$
$(e_g)^2\,(b_{2g})^2$	6	1			1			1			1						$(e_g)^2\,(a_{1g})^2\,(b_{1g})^2$
$(a_{1g})^2\,(b_{1g})\,(b_{2g})$	4				1	1											$(e_g)^4\,(b_{1g})\,(b_{2g})$
$(b_{1g})^2\,(a_{1g})\,(b_{2g}$	4										1	1					$(e_g)^4\,(a_{1g})\,(b_{2g})$
$(b_{2g})^2\,(a_{1g})\,(b_{1g})$	4							1	1								$(e_g)^4\,(a_{1g})\,(b_{1g})$
$a_{1g})^2\,(e_g)\,(b_{1g})$	8													1	1		$(e_g)^3\,(b_{1g})\,(b_{2g})^2$
$(a_{1g})^2\,(e_g)\,(b_{2g})$	8													1	1		$(e_g)^3\,(b_{1g})^2\,(b_{2g})$
$(b_{1g})^2\,(e_g)\,(a_{1g})$	8													1	1		$(e_g)^3\,(a_{1g})\,(b_{2g})^2$
$(b_{1g})^2\,(e_g)\,(b_{2g})$	8													1	1		$(e_g)^3\,(a_{1g})^2\,(b_{2g})$
$(b_{2g})^2\,(e_g)\,(a_{1g})$	8													1	1		$(e_g)^3\,(a_{1g})\,(b_{1g})^2$
$(b_{2g})^2\,(e_g)\,(b_{1g})$	8													1	1		$(e_g)^3\,(a_{1g})^2\,(b_{1g})$
$(e_g)^2\,(a_{1g})\,(b_{1g})$	24	1	1		1	1		1	1		1	2	1				$(e_g)^2\,(a_{1g})\,(b_{1g})\,(b_{2g})^2$
$(e_g)^2\,(a_{1g})\,(b_{2g})$	24	1	1		1	1		1	2	1	1	1					$(e_g)^2\,(a_{1g})\,(b_{1g})^2\,(b_{2g})$
$(e_g)^2\,(b_{1g})\,(b_{2g})$	24	1	2	1	1	1		1	1		1	1					$(e_g)^2\,(a_{1g})^2\,(b_{1g})\,(b_{2g})$
$(a_{1g})\,(b_{1g})\,(b_{2g})\,(e_g)$	32													2	3	1	$(e_g)^3\,(a_{1g})\,(b_{1g})\,(b_{2g})$

the corresponding d^{10-n} configurations are displayed. The splitting products of the strong field configurations are, of course, equal regarding their numbers and multiplicities to the splitting products of the RUSSEL—SAUNDERS terms.

§ 4. *Some generalizing remarks*

Considering the even character of the functions used the above results are directly transmissible by omitting the suffix g to the cases of complex fields possessing symmetries D_4, C_{4v} and D_{2d} too. The above considerations

* In the third column the numbers 1, 3 and 5 mean the multiplicities of the terms.

Table V*

d^5	Total sum of *d. n.*	A_{1g}			A_{2g}			B_{1g}			B_{2g}			E_g		
		2	4	6	2	4	6	2	4	6	2	4	6	2	4	6
$(e_g)^4\,(a_{1g})$	2	1														
$(e_g)^4\,(b_{1g})$	2							1								
$(e_g)^4\,(b_{2g})$	2										1					
$(e_g)^3\,(a_{1g})^2$	4													1		
$(e_g)^3\,(b_{1g})^2$	4													1		
$(e_g)^3\,(b_{2g})^2$	4													1		
$(a_{1g})^2\,(b_{1g})^2\,(b_{2g})$	2										1					
$(a_{1g})^2\,(b_{2g})^2\,(b_{1g})$	2							1								
$(b_{1g})^2\,(b_{2g})^2\,(a_{1g})$	2	1														
$(a_{1g})^2\,(b_{1g})^2\,(e_g)$	4													1		
$(a_{1g})^2\,(b_{2g})^2\,(e_g)$	4													1		
$(b_{1g})^2\,(b_{2g})^2\,(e_g)$	4													1		
$(e_g)^2\,(a_{1g})^2\,(b_{1g})$	12	1			1			1			1	1				
$(e_g)^2\,(a_{1g})^2\,(b_{2g})$	12	1			1			1	1		1					
$(e_g)^2\,(b_{1g})^2\,(a_{1g})$	12	1			1	1		1			1					
$(e_g)^2\,(b_{1g})^2\,(b_{2g})$	12	1			1			1	1		1					
$(e_g)^2\,(b_{2g})^2\,(a_{1g})$	12	1			1	1		1			1					
$(e_g)^2\,(b_{2g})^2\,(b_{1g})$	12	1			1			1			1	1				
$(a_{1g})^2\,(b_{1g})\,(b_{2g})\,(e_g)$	16													2	1	
$(b_{1g})^2\,(a_{1g})\,(b_{2g})\,(e_g)$	16													2	1	
$(b_{2g})^2\,(a_{1g})\,(b_{1g})\,(e_g)$	16													2	1	
$(e_g)^2\,(a_{1g})\,(b_{1g})\,(b_{2g})$	48	3	3	1	2	1		2	1		2	1				
$(e_g)^3\,(a_{1g})\,(b_{1g})$	16													2	1	
$(e_g)^3\,(a_{1g})\,(b_{2g})$	16													2	1	
$(e_g)^3\,(b_{1g})\,(b_{2g})$	16													2	1	

naturally do not depend on the concrete form of the function system used in a given approximation. In the course of the calculations group theoretical considerations were adapted everywhere. Thus the results obtained are quite exact. For the explanation of the spectra of diamagnetic and anomalously paramagnetic complexes this method of strong field approximation can be used with good results. According to PAULING the diamagnetic complexes are covalent, hence according to the statement of STEVENS [17] the strong

* In the third column the numbers 2, 4 and 6 mean the multiplicities of the terms.

field model can be regarded to be formally equivalent to the covalent model. Consequently the given results can be used in a wide circle of complexes.

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