901. *The Splitting of Terms by Low-symmetry Ligand-field Components*

By B. N. Figgis

The splitting, Δ, between the orbital components of the cubic field terms of *d*-electron configurations is derived as a function of the positions of the ligand atoms and the strength of the primary cubic ligand-field they create at the central metal atom. The splitting arises from the presence of a component of tetragonal or trigonal symmetry in the ligand-field. This theory is applied in a semi-quantitative manner to the tervalent ions of the elements Ti–Mn in solid solution in alumina, with the assumption that the trigonal ligand-field component is of the same magnitude in each ion. The sign of the splittings of the terms of these ions is reproduced, and their relative magnitudes are given mostly within a factor of two.

THE orbital degeneracy of *T*- and *E*-terms in a cubic ligand-field is lifted by components of lower symmetry.[1,2] Detailed investigations of the spectra, magnetic and electron spin resonance properties of complexes of transition elements must take this splitting into account.[3-8] Very often, it is sufficient to assume that the symmetry is reduced from cubic only to tetragonal or trigonal; then the energy levels of the term, in the absence of other perturbations, can be expressed in simple form. A *T*-term is split into components, one orbitally non-degenerate, one of two-fold orbital degeneracy. The splitting of the term is conveniently specified by the parameter Δ, which is the energy separation between the two components. The position is summarised in the Figure, where the splitting of a ${}^3T_{1g}$-term on reduction of the symmetry to tetragonal is shown. Δ is defined as positive when the orbital singlet lies lowest.[7] An *E*-term is split into two orbital singlets, separated by Δ. An arbitrary definition of the sign of Δ in this case is introduced later.

The crystal-field potential for an octahedron of charges, distorted by extension or compression along a four-fold axis, is

$$V_{\text{tetrag}} = A_4[Y_4^0 + (\tfrac{5}{14})^{\frac{1}{2}}(Y_4^4 + Y_4^{-4})] + A_2Y_2^0. \qquad (1)$$

In this formula the first term is of cubic symmetry, the second term introduces the tetragonal ligand-field component. Such a distortion reduces the symmetry from O_h to D_{4h}. The axis of the distortion is defined as the *Z*-direction. This potential also suffices for a tetrahedron of charges, distorted by extension or compression along a two-fold axis.

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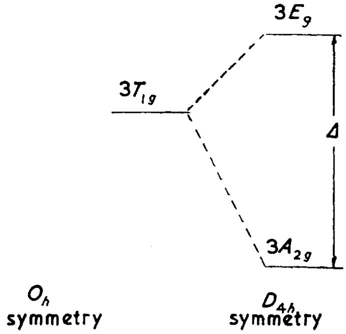
[1] H. Bethe, *Ann. Phys.*, 1929, **3**, 133.
[2] W. G. Penney and R. Schlapp, *Phys. Rev.*, 1932, **42**, 666.
[3] M. L. H. Pryce and W. A. Runciman, *Discuss. Faraday Soc.*, 1958, **26**, 34.
[4] D. S. McClure, *Solid State Phys.*, 1959, **9**, 399.
[5] K. D. Bowers and J. Owen, *Reports Progr. Phys.*, 1955, **18**, 304.
[6] D. Polder, *Physica*, 1942, **9**, 709.
[7] B. N. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 204.
[8] A. Siegert, *Physica*, 1937, **4**, 138.

Then the symmetry is reduced from T_d to D_{2d}. For a cube so distorted the symmetry is reduced to D_{4h}.

The crystal-field potential for an octahedron of charges distorted by extension or compression along a three-fold axis is [9]

$$V_{\text{trig}} = A_4'[Y_4^0 + (\tfrac{10}{7})^{\frac{1}{2}}(Y_4^3 + Y_4^{-3})] + A_2'Y_2^0. \qquad (2)$$

Again, the axis of distortion is defined as the Z-direction. The distortion reduces the symmetry from O_h to D_{3d}. This potential also suffices for a cube, or a tetrahedron, distorted along a three-fold axis.



The splitting of the ${}^2T_{1g}$ term of d^2 upon the reduction of the symmetry from octahedral to tetragonal

The formulæ of equations (1) and (2) are the most suitable forms with which to perform calculations. They may be rewritten as functions of the Cartesian co-ordinates, in which form they are rather easier to picture. *Both* the potentials can be put in the form [2]

$$V_{(\text{tetrag or trig})} = D(x^4 + y^4 + z^4 - 3r^4/5) + C(z^2 - r^2/3). \qquad (3)$$

The term in D introduces the main cubic ligand-field, that in C the tetragonal or trigonal component. This form of the potential is responsible for the common notation for the ligand-field parameter, Dq. D is the constant in the potential: q is a number such that the matrix elements

$$\langle(m_l)\,|\,x^4 + y^4 + z^4 - 3r^4/5\,|\,(m_l')\rangle$$

are integral multiples of it. In fact, $q = 2\overline{r^4}/105$. (m_l) indicates a d-orbital wave-function specified by the appropriate value of m_l.

The parameter Dq is very convenient, because the splittings of free-ion F- and D-terms in a weak cubic ligand-field are integral multiples of it.[2] However, it may be noted that stronger ligand fields do not split F-terms into integral multiples of Dq.[8,10,11] Here, a ligand-field is defined as weak if it splits free-ion terms by an amount small compared to the separations between them.[12]

Similarly, it is possible to introduce a quantity, p, such that the matrix elements

$$\langle(m_l)\,|\,z^2 - r^2/3\,|\,(m_l')\rangle$$

are simple multiples of it. Then the parameter Cp takes on the same role for the splitting of cubic-field T- and E-terms by a tetragonal or trigonal component that Dq has for the splitting of the free-ion terms, F and E, by the main cubic field.

The purpose of this Paper is to point out the relationship between the quantities Δ and Cp.

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[9] W. Moffitt, *J. Chem. Phys.*, 1956, **25**, 1189.

[10] B. N. Figgis, M. Gerloch, and R. Mason, *Proc. Roy. Soc.*, 1964, *A*, **279**, 210.

[11] L. E. Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

[12] B. N. Figgis, *Nature*, 1958, **182**, 1568.

The Calculations.—The matrix elements of equation 4 are:[13]

$$\langle(0)|\,(z^2 - r^2/3)\,|(0)\rangle = (4/21)\overline{r^2} = 4p$$

$$\langle(\pm1)|\,(z^2 - r^2/3)\,|(\pm1)\rangle = (2/21)\overline{r^2} = 2p$$

$$\langle(\pm2)|\,(z^2 - r^2/3)\,|(\pm2)\rangle = (-4/21)\overline{r^2} = -4p$$

$$\langle(m_l)|\,(z^2 - r^2/3)\,|(m_l')\rangle = 0,\ m_l' = m_l$$

$$p = \overline{r^2}/21.$$

In order to find the effect of the potential $C(z^2 - r^2/3)$ on the wave-functions of T- and E-terms, it is necessary to have these available as linear combinations of the single-electron wave-functions, (m_l). The combinations for the ^2D term of d^1 and the ^3F and ^3P terms of d^2 are given below. $\langle L, M_L\rangle$ specifies that orbital wave-function of a free-ion term specified by the quantum numbers L and M_L. (m_l, m_l') indicates a Slater determinental wave-function for two d-electrons of quantum numbers m_l and m_l'.

d^1; ^2D:

$$\langle 2, M_L\rangle = (m_l).$$

d^2; ^3F:

$$\langle 3, 0\rangle = 5^{-\frac{1}{2}}(2, -2) + (4/5)^{\frac{1}{2}}(1, -1)$$

$$\langle 3, \pm1\rangle = \pm(3/5)^{\frac{1}{2}}(\pm2, \mp1) \pm (2/5)^{\frac{1}{2}}(\pm1, 0)$$

$$\langle 3, \pm2\rangle = \pm(\pm2, 0)$$

$$\langle 3, \pm3\rangle = \pm(\pm2, \pm1).$$

^3P

$$\langle 1, 0\rangle = (4/5)^{\frac{1}{2}}(2, -2) - 5^{-\frac{1}{2}}(1, -1)$$

$$\langle 1, \pm1\rangle = \pm(2/5)^{\frac{1}{2}}(\pm2, \mp1) \mp (3/5)^{\frac{1}{2}}(\pm1, 0)$$

The linear combinations of free-ion $\langle L, M_L\rangle$ wave-functions for the terms in a cubic ligand-field have been given relative to both the tetragonal and trigonal axes of an octahedron or tetrahedron.[13] For the present purposes, it is convenient to use them in slightly different form. They are given in Table 1. It is shown below that a derivation of the results for the d^1- and d^2-configurations is sufficient.

TABLE 1

The linear combinations of free-ion $\langle L,M_L\rangle$ wave-functions for cubic-field terms arising from the d^1- and d^2-configurations

Free-ion term	Cubic-field term	Tetragonal axis	Trigonal axis
^2D	$^2T_{2g}$	$2^{-\frac{1}{2}}[\langle 2, 2\rangle - \langle 2, -2\rangle]$ $\langle 2, \pm1\rangle$	$\langle 2, 0\rangle$ $3^{-\frac{1}{2}}[2^{\frac{1}{2}}\langle 2, \pm2\rangle \mp \langle 2, \mp1\rangle]$
	^2E_g	$\langle 2, 0\rangle$ $2^{-\frac{1}{2}}[\langle 2, 2\rangle + \langle 2, -2\rangle]$	$3^{-\frac{1}{2}}[\langle 2, \pm2\rangle \pm 2^{\frac{1}{2}}\langle 2, \mp1\rangle]$
^3F	$^3T_{1g}$	$\langle 3, 0\rangle$ $24^{-\frac{1}{2}}[15^{\frac{1}{2}}\langle 3, \pm3\rangle - 3\langle 3, \mp1\rangle]$	$6^{-\frac{1}{2}}[5^{\frac{1}{2}}\langle 3, \pm2\rangle \pm \langle 3, \mp1\rangle]$ $3^{-1}[2\langle 3, 0\rangle - (5/2)^{\frac{1}{2}}(\langle 3, 3\rangle - \langle 3, -3\rangle)]$
	$^3T_{2g}$	$2^{-\frac{1}{2}}[\langle 3, 2\rangle + \langle 3, -2\rangle]$ $24^{-\frac{1}{2}}[3\langle 3, \pm3\rangle + 15^{\frac{1}{2}}\langle 3, \mp1\rangle]$	$2^{-\frac{1}{2}}[\langle 3,3\rangle + \langle 3, -3\rangle]$ $6^{-\frac{1}{2}}[3\langle 3, \pm2\rangle \mp 5^{\frac{1}{2}}\langle 3, \mp1\rangle]$
^3P	$^3T_{1g}$	$\langle 1, 0\rangle$ $\langle 1, \pm1\rangle$	$\langle 1, 0\rangle$ $\langle 1, \pm1\rangle$

E_g Terms.—The evaluation of the effect of the potential $C(z^2 - r^2/3)$ on the orbital wave-functions of the E_g-term of d^1 is straightforward. The wave-function $\langle 2, 0\rangle$ lies at

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[13] B. Bleaney and K. W. H. Stevens, *Reports Progr. Phys.*, 1953, **16**, 108.

$4Cp$, $2^{-\frac{1}{2}}[\langle 2, 2\rangle + \langle 2, -2\rangle]$ at $-4Cp$, for the tetragonal distortion. The two wave-functions for the trigonal axis have zero matrix element under the potential; the term is *not* split by a trigonal component.[14] For E-terms there is no obvious way of assigning the sign of the term splitting, Δ. Arbitrarily, I define Δ as positive for the tetragonal case when the wave-function $\langle 2, 0\rangle$ is the lower. Then $\Delta = -8Cp$.

The results for other E_g-terms which arise from D free-ion ground-terms may be obtained from this result by treating " holes " in a filled e_g orbital set as " positive electrons " and hence inverting the sign of the matrix elements. The technique is the same as that employed for deducing the splitting of free-ion ground-terms by weak cubic ligand-fields. In that connexion the results for higher numbers of d-electrons are obtained from the splitting of the ^2D term of d^1 and the ^3F-term of d^2. The splitting for d^{5+n} is the same as for d^n; the splitting for d^{5-n} and d^{10-n} is inverted relative to d^n: $n = 1$ or 2. Also, there is an inversion of the splitting pattern of cubic-field free-ion terms on passing from octahedral to tetrahedral symmetry.[15] A similar inversion holds for the splitting pattern of E_g and other terms under the potential $C(z^2 - r^2/3)$, in that C changes sign for the same deformation of a cube, on passing to the inscribed octahedron (see below).

The results for the E_g-terms from the D ground-terms of the configurations d^1, d^4, d^6, and d^9 are summarised in Table 2.

T_{2g} *Terms.*—The evaluation of the effect of the potential $C(z^2 - r^2/3)$ on the wave-functions of the $^2T_{2g}$-term of d^1 is also straightforward. In tetragonal symmetry the wave-function $2^{-\frac{1}{2}}[\langle 2, 2\rangle - \langle 2, -2\rangle]$ lies at $-4Cp$, the two wave-functions $\langle 2, \pm 1\rangle$ lie at $2Cp$. When the distortion is down the three-fold axis, the wave-function $\langle 2, 0\rangle$ lies at $4Cp$, the two wave-function $3^{-\frac{1}{2}}[2^{\frac{1}{2}}\langle 2, \pm 2\rangle \mp \langle 2, \mp 1\rangle]$ lie at $-2Cp$. Thus

$$\Delta_{\text{tetrag}} = 6Cp, \quad \Delta_{\text{trig}} = -6Cp.$$

For the $^3T_{2g}$-term of d^2, in tetragonal symmetry, the matrix elements of $C(z^2 - r^2/3)$ are zero for each of the three wave-functions. In trigonal symmetry, the wave-function $2^{-\frac{1}{2}}[\langle 3, 3\rangle + \langle 3, -3\rangle]$ lies at $-2Cp$, the two wave-functions $6^{-\frac{1}{2}}[\langle 3, \pm 2\rangle \mp 5^{\frac{1}{2}}\langle 3, \pm 1\rangle]$ at Cp. Hence

$$\Delta_{\text{tetrag}} = 0, \quad \Delta_{\text{trig}} = 3Cp.$$

The results for T_{2g}-terms from other D and F ground-terms are obtained by considering the inversions which take place for " holes " in a filled t_{2g} shell, and for tetrahedral symmetry. They are summarised in Table 2. The result for the $^2T_{2g}$-term of the spin-paired configuration t_{2g}^5 can also be obtained by the same arguments and is included in the Table. The magnitude of its splitting follows the $^2T_{2g}$-term of d^1.

TABLE 2

The sign of the splitting, Δ, of terms of the same multiplicity as the ground-term, for the various d-electron configurations. The signs are given relative to those for the same terms, neglecting multiplicity, of the configuration d^1 (d^4, d^5, d^6, d^9) or d^2 (d^3, d^4, d^7, d^8)

Term	Configuration:	d^3	d^4	d^5	d^6	d^7	d^8	d^9
E_g			—		+			—
T_{1g}		—	—*			+	—	
T_{2g}		—	—	—†	+	+	—	—

* $^3T_{1g}$ term of d^4, $c = -\frac{1}{2}$. † $^2T_{2g}$ term of t_{2g}^5.

T_{1g} *Terms.*—The position for T_{1g}-terms is more complicated, because cubic ligand-fields of varying strength must be dealt with. In Table 1 the linear combinations of free-ion wave-functions for the two $^3T_{1g}$-terms of d^2 in a *weak* ligand-field are listed. At higher ligand-field strengths these combinations no longer apply. The wave-functions for the terms approach (—, ± 1) and (1, -1) etc., as the strength increases. Here I have used

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[14] B. Bleaney, K. D. Bowers and R. S. Trenam, *Proc. Roy. Soc.*, 1955, *A*, **228**, 157.

[15] C. J. Gorter, *Phys. Rev.*, 1932, **42**, 437.

(—) to denote the wave-function $2^{-\frac{1}{2}}[(2) - (-2)]$. These wave-functions correspond to the configuration t_{2g}^2 or $t_{2g}^1 \cdot e_g^1$.

For ligand-fields of intermediate strength, where the spliting of free-ion terms is of the same magnitude as the separations between them, the ${}^3T_{1g}$-term wave-functions of d^2 are intermediate between those of Table 1 and the configurations t_{2g}^2 and $t_{2g}^1 \cdot e_g^1$. They are conveniently expressed as linear combinations of the weak-field term wave-functions.[10] The ground ${}^3T_{1g}$-term, which belongs to the free-ion F-term in a weak ligand-field, gives

$$\Psi'^{\mathrm{F}}({}^3T_{1g}) = (1 + c^2)^{-\frac{1}{2}}\{\Psi'[{}^3T_{1g}^{\mathrm{O}}(\mathrm{F})] + c\Psi'[{}^3T_{1g}^{\mathrm{O}}(\mathrm{P})]\},$$

or, more specifically, for tetragonal symmetry,

$$\Psi'^{\mathrm{F}}({}^3T_{1g})\begin{cases}(1 + c^2)^{-\frac{1}{2}}[\langle 3, 0\rangle + c\langle 1, 0\rangle] \\ (1 + c^2)^{-\frac{1}{2}}[24^{-\frac{1}{2}}(15^{\frac{1}{2}}\langle 3, \pm 3\rangle + 3\langle 3, \mp 1\rangle) + c\langle 1, \mp 1\rangle].\end{cases}$$

The equivalent wave-functions for trigonal symmetry are readily obtained from Table 1. c is defined by the equation

$$c = (6Dq + E)/4Dq.$$

with E the lower root of the equation

$$E^2 + (6Dq - 15B)E - 16D^2q^2 - 90DqB = 0.$$

B is the parameter for interelectronic repulsion. The ${}^3F$—${}^3P$ separation is $15B$. c is zero at the limit of a weak ligand-field: it is $-\frac{1}{2}$ at the limit of strong ligand-fields.

The higher ${}^3T_{1g}$-term, which belongs to the free-ion P-term in a weak ligand-field, gives,

$$\Psi'^{\mathrm{P}}({}^3T_{1g}) = (1 + c^2)^{-\frac{1}{2}}[c\Psi'{}^3T_{1g}^{\mathrm{O}}(\mathrm{F}) - \Psi'{}^3T_{1g}^{\mathrm{O}}(\mathrm{P})]$$

The evaluation of the effect of the potential $C(z^2 - r^3/3)$ on the wave-functions $\Psi'^{\mathrm{F}}({}^3T_{1g})$ and $\Psi'^{\mathrm{P}}({}^3T_{1g})$ is summarised in Table 3.

TABLE 3

The splitting parameter, Δ, for the potential $C(z^2 - r^2/3)$ acting on the wave-functions of the ${}^3T_{1g}$ terms of d^2

	Tetragonal symmetry			Trigonal symmetry		
Wave-function	General result	Weak-field limit, $c = 0$	Strong-field limit, $c = -\frac{1}{2}$	General result	Weak-field limit, $c = 0$	Strong-field limit, $c = -\frac{1}{2}$
$\Psi'^{\mathrm{F}}{}_3(T_{1g})$	$[6(7c^2 + 12c - 2)/5(1 + c^2)]Cp$	$-2{\cdot}4Cp$	$-6Cp$	$[3(14c^2 - 16c + 1)/5(1 + c^2)]Cp$	$0{\cdot}6Cp$	$6Cp$
$\Psi'^{\mathrm{P}}{}_3(T_{1g})$	$[6(-2c^2 - 12c + 7)/5(1 + c^2)]Cp$	$8{\cdot}4Cp$	$12Cp$	$[3(c^2 + 16c + 14)/5(1 + c^2)]Cp$	$8{\cdot}4Cp$	$3Cp$

The results for the T_{1g}-terms of other configurations are given in Table 2. In that Table, the entry under the configuration d^4 applies to only the ${}^3T_{1g}$-term of t_{2g}^4. Since the ligand-field must be strong to force the spin-pairing, c may be taken to be $-\frac{1}{2}$ in this connexion. This ${}^3T_{1g}$-term does not arise from a free-ion F- or P-term, so that c cannot be evaluated by the methods used above.

The Relationship between the Sign of C *and Molecular Geometry.*—The sign of the constant C is derived from the molecular geometry by a further consideration of equations (1) and (2). The constant A_2' in equation (1) is, on the crystal-field model of an octahedron, deformed along a four-fold axis,

$$A_2' = 2(2\pi)^{\frac{1}{2}}(2/5)^{\frac{1}{2}}(a^{-3} - b^{-3})zer^2.$$

Here, ze is the negative charge assigned to the ligand atoms, two of which are diametrically opposite at a distance b from the centre and four are in the plane at a distance a. Then

$$C = 3ze(a^{-3} - b^{-3}).$$

For $b < a$ the octahedron is compressed along the C_4-axis, giving " positive tetragonality "[1]: C is positive. For $b > a$, an octahedron extended along the C_4-axis to give " negative tetagonality," C is negative. For a tetrahedron deformed along an S_4-axis, a tetragonal distortion,

$$A_2 = 4 \,.\, (2\pi)^{\frac{1}{2}} \,.\, 10^{-\frac{1}{2}} \,.\, (3 \cos^2 \alpha - 1) \,.\, zer^2a^{-3}:$$
$$C = 3zea^{-3}(3 \cos^2\alpha - 1).$$

C is positive for an elongation of the tetrahedron ($\alpha < \cos^{-1}(3^{-\frac{1}{2}})$). α is the angle subtended at the centre by a vertex and the S_4-axis. Similarly, C is positive for the elongation of a cube along a C_4-axis.

The deformation of an octahedron along a trigonal axis leads to

$$C = \tfrac{9}{2}(3 \cos^2 \alpha - 1)zea^{-3}.$$

C is positive for extension [$\alpha < \cos^{-1}(3^{-\frac{1}{2}})$]. The deformation of a tetrahedron or a cube along the same axis cannot be described so simply. If the action on the tetrahedron is the spreading out of the ligands off the three-fold axis to give C_{3v} symmetry, C is negative. The compression of two opposite corners of a cube, leading to D_{3d} symmetry, gives C positive.

Two other deformations of an octahedron in relationship to the trigonal axis may also be considered. " Twisting " of the octahedron about this axis, so that one of the triangular faces ceased to be out of phase by π with the other face, generates a potential composed only of the odd spherical harmonics and consequently does not interact with the d wave-functions.[1] A displacement of the octahedron along the C_3-axis relative to the central ion gives C_{3v} symmetry. It generates a potential which contains, as well as expressions in the odd spherical harmonics, the term in Y_2^0 with (see equation 2)

$$A_2' = (36/5)(2\pi)^{\frac{1}{2}}(5/8)^{\frac{1}{2}} \,.\, ze\varepsilon^2r^2/a^5,$$

ε, a distance small compared to a, is the displacement of the central atom relative to the octahedron. Thus, C,

$$C = \tfrac{27}{2}\, \varepsilon^2zea^{-5},$$

is always positive.

DISCUSSION

Insufficient accurate structural data are available at present on paramagnetic complexes of the transition metals to permit the extensive quantitative application of the above theory. In effect, a portion of the theory has been used in a quantitative manner.[10] The rapid progress taking place in the determination of such structures should make it more useful in the near future. Meanwhile, some general remarks may be made on its significance, and a semiquantitative application to certain ions in corundum undertaken.

The general point which emerges is that a correlation between Δ and properties of an ion other than the details of the ligand distribution around it is not likely to be found. In some instances the sign of Δ for a somewhat similar type of distortion of the ligand environment from cubic symmetry depends on the symmetry (tetragonal or trigonal) of the distortion. Furthermore, for T_{1g}-terms, given a knowledge of such details, their correlation with Δ requires that the strength of the primary cubic ligand-field relative to the inter-electronic repulsions be taken into account. This is seen by reference to Table 3, where Δ for one of the $^3T_{1g}$-terms varies from 0·6 to 6 units, for a given trigonal component, as the strength of the cubic field varies from weak to strong.

There is evidence [10] that in substantially ionic environments such as in $CoCl_4^{2-}$, Δ may be correlated in a semiquantitative fashion with the details of the departure of the ligand environment from cubic symmetry; in those complex ions the distortion is primarily of tetragonal symmetry. The spectra of a number of tervalent ions in solid solution in alumina (corundum) have been interpreted, including the magnitudes of the low-symmetry splittings of the cubic-field terms.[16-19] Estimates of the splitting of the ground-term have been obtain from studies of the magnetic susceptibilities of those system.[20-22] I refer here mainly to the work of McClure.[16] In these systems, the approach to the ionic model of the ligand-field effect is likely to be closer than for the tetrachloro-complexes. Since the transition-metal ion is in solid solution, its exact position in relation to the octahedron of O^{2-} ions which surrounds it cannot be known. However, like the Al^{3+} ion which it replaces, it must lie on the C_3-axis, but displaced from the centre at a position of approximately C_{3v} symmetry. The relationship between Δ and the position of the transition-metal ion relative to its octahedron has been discussed [16,18,20] on the basis of a site symmetry lower than C_{3v}, in the cubic weak-field limit. The only general conclusions that can be drawn from these treatments is that the low-symmetry ligand-field component approximates to trigonal symmetry, and has a value which is compatible with an environment close to that of the Al^{3+} ion, but with the ion shifted somewhat along the C_3-axis.

If consideration of the site-symmetry for the transition-metal ion in alumina is restricted to C_{3v}, but account is taken of the strength of the octahedral ligand-field, a semi-quantitative description of the results can be obtained. Attention is restricted to the ions for which the data are available, *i.e.*, Ti^{3+}, V^{3+}, Cr^{3+}, and Mn^{3+}. It is assumed that each of the ions is surrounded by the same O^{2-} environment, and has the same value of Cp. Obviously, because of the differing radii of the tervalent ions, the assumption cannot be fully valid. The lack of a knowledge of effective values for $\overline{r^4}$ and $\overline{r^2}$ for transition-metal ions has in general prevented quantitative estimates of Dq and Cp for them being obtained from first principles. However, Dq, which depends directly on $\overline{r^4}$, changes little from ion to ion in this series (see Table 4). It seems reasonable to suppose that Cp, which depends on $\overline{r^2}$, also should not change much for the series. The following treatment makes no attempt to calculate the absolute value of Δ. From the molecular geometry, C is required to be positive. Rather the relative values of Δ for the terms of the series of ions are compared. The values of Dq and B evaluated from the spectra of the ions in alumina are included in Table 4.

TABLE 4

The comparison of Δ obtained experimentally [3,16,18-21] and calculated for the terms of the ions Ti^{3+}—Mn^{3+} in alumina. Included are values of quantities relevant to the calculations. Trigonal symmetry is assumed $s = \Delta/\Delta_{(^3T_{1g}(F),\, V^{3+})}$

Ion	Dq (cm.$^{-1}$)	B (cm.$^{-1}$)	c	Term	Δ_{obs} (cm.$^{-1}$)	s_{obs}	s_{calc}
Ti^{3+}	1900	—	—	$^2T_{2g}(D)$	$-{>}500$	$-{>}0·5$	$-1·4$
				$^2E_g(D)$	(0) *	(0) *	0
V^{3+}	1750	540	$-0·335$	$^3T_{1g}(F)$	960	1	1
				$^3T_{2g}(F)$	(90) *	(0·1) *	0·7
				$^3T_{1g}(P)$	380	0·4	1·1
Cr^{3+}	1815	650	$-0·32$	$^4T_{2g}(F)$	-450	$-0·5$	$-0·7$
				$^4T_{1g}(F)$	-400	$-0·4$	$-0·4$
				$^4T_{1g}(P)$	-800	$-0·9$	$-0·8$
Mn^{3+}	1900	—	—	$^5T_{2g}(D)$	1900	2·0	1·4

* See text.

In Table 4 the values of Δ for the terms of the same multiplicity as the ground term for the trivalent ions of the elements Ti–Mn, as determined from the spectra and magnetic behaviour, are listed. They are also listed as their ratio to the value of Δ for the $^3T_{1g}(F)$-term of V^{3+} defined as unity. The value of the same ratio calculated from the preceding

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theory with constant Cp is given for each ion. For V^{3+} and Cr^{3+}, which give rise to T_{1g}-terms, the value of the constant c, determined from Dq and B, and from which the ratio is calculated, is included.

Table 4 shows that the main features of the trigonal splitting of the terms of the ions are reproduced by the theory. The ${}^3T_{1g}$(F)-term of V^{3+}, for example, is split with positive sign as demanded by the fact that C is positive. The splitting for other terms is reversed in sign relative to the ${}^3T_{1g}(F)(V^{3+})$-term when required, and is mostly within a factor of two of the predicted value. The agreement is particularly good for the three bands of Cr^{3+}. The exception to the success of the theory lies in the ${}^3T_{2g}$(F)-term of V^{3+} and to a lesser extent the ${}^2E_g$-term of Ti^{3+}. The splitting of those terms evidently do not reflect the ligand environment accurately, since it corresponds to tetragonal rather than trigonal symmetry. It has been suggested [16] that they are subject to a strong Jahn–Teller perturbation in addition to the trigonal crystal-field component. The agreement between theory and experiment cannot be expected to be better, in view of the approximations made in its application to the system.

The importance of taking the present theory into account in discussing the splittings of terms in transition-metal complex compounds has been pointed out in a general manner previously.[23]

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