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## On the Energy Levels of Chrome Alum

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The energy levels for the configuration  $d^3$  of the chrome ion in chrome alum are calculated by starting with the empirical spectroscopic data on the free  $\text{Cr}^{+++}$  ion, and then making the assumption that the interatomic forces in the solid state can be represented by a crystalline potential of cubic symmetry, whose magnitude is taken from Schlapp and Penney's theory of the magnetic susceptibility. The particular point to be tested is whether in the solid there is a doublet level only  $15,000\text{ cm}^{-1}$  above the basic quartet state, as predicted in the preceding paper from the study of Spedding and Nutting's data on the Zeeman effect. The computed deepest doublet is about  $18,200\text{ cm}^{-1}$  higher than the ground level, but the discrepancy is not excessive in view of uncertainties in the parameters of the crystalline field and the fact that any "one-atom" model is only an approximation in the solid state. As already suggested by Spedding and Nutting, it is very essential in computing the positions of *excited* levels, to include elements of the crystalline potential which are nondiagonal in the quantum number  $L$ , for without them the lowest doublet is much too high, *viz.*  $30,000\text{ cm}^{-1}$  above the ground term. On the other hand, the effect of these nondiagonal members is shown to be unimportant for the *ground* level of greatest multiplicity, not merely for  $\text{Cr}^{+++}$  but also for other salts of the iron group, so that previous calculations by various writers on magnetic susceptibilities are not appreciably impaired by their assumption of Russell-Saunders coupling.

### INTRODUCTION

USUALLY the spectra of solids are characterized by continuous bands rather than discrete lines. Sharp lines, however, are sometimes observed in salts of the iron or rare earth groups, associated with transitions of electrons in incomplete inner shells. Comparatively little has been done in studying these lines theoretically, although the problem is obviously much simpler than that of the energy bands associated with conduction electrons. The comparative simplicity arises from the fact that the electrons may, at least approximately, be regarded as remaining on the same atom, and the interatomic forces may be represented by a crystalline potential. We thus have a one-atom problem, rather than a dynamical system involving infinitely many atoms.

It is the purpose of the present paper to consider the case of potassium chrome alum ( $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ). Most of the energy levels belonging to the configuration  $3d^3$  of the free  $\text{Cr}^{+++}$  ion are known from ordinary spectroscopic measurements, and we shall endeavor to estimate the corresponding positions of the levels in solid chrome alum. In the latter, the ion is subject to a field of dominantly cubic character, whose potential may, without loss of generality,<sup>1</sup> be taken to be

$$V = \sum_i V_i \quad \text{with} \quad V_i = D[x_i^4 + y_i^4 + z_i^4 - \frac{3}{2}r_i^4] + f(r_i). \quad (1)$$

The sum in (1) is over the three  $3d$  electrons. The additive term  $f(r_i)$  will vanish if the potential satisfies Laplace's equation, as we shall henceforth assume. Very likely it does not do so, but the resulting correction is merely an additive constant common to all levels of the configurations  $3d^3$  and so is of no importance for us.

It will be necessary to calculate only the energy levels belonging to the configuration  $3d^3$ , for orbits associated with other configurations are not sufficiently sequestered in the interior of the atom to give rise to sharp lines, and also usually involve too high an energy to be involved in absorption lines in the optical region. The observed lines are thus internal to the configuration  $3d^3$ , and so violate the Laporte rule, as discussed in the preceding paper.

<sup>1</sup>The generality results because higher harmonics than those of the fourth degree in development of the crystalline potential make no contribution for  $d$  electrons. See, for instance footnote 4 of J. H. Van Vleck, *J. Chem. Phys.* **7**, 61 (1939).

It is not necessary for us to include the modifications of the energy levels resulting from spin-orbit coupling, or from the fact that, strictly speaking, the crystalline potential has trigonal rather than perfectly cubic symmetry, for we only endeavor to locate the energy levels to within an error of the order  $10^3 \text{ cm}^{-1}$ . This is sufficient accuracy to answer the question as to whether it is reasonable that there be doublet levels  $15,000 \text{ cm}^{-1}$  above the ground level state, as predicted in the previous paper from the study of the Zeeman measurements of Spedding and Nutting. To essay higher accuracy would be presumptuous in view of the qualitative and provisional nature of existing models of forces in solid salts.

In the ordinary Penney-Schlapp theory<sup>2</sup> of magnetic ions in the solid state, elements of the crystalline potential which are nondiagonal in the quantum number  $L$  are neglected. This approximation is equivalent to assuming that  $L$  is a good quantum number. This supposition is not warranted in the case of the doublet states of chrome alum, although we shall later see (cf. end of article) that it is reasonably adequate for the quartets, and in particular the ground state  $d^3 \text{ } ^4F\Gamma_2$  involved in determinations of the magnetic susceptibility. Spectroscopic measurements, however, can involve excited doublet states, and so we must allow for the breakdown of  $L$  coupling, and so consider matrix elements nondiagonal in  $L$ . We shall, however, neglect elements of the crystalline potential nondiagonal in the principal quantum number  $n$ . Such elements express the fact that this potential blends  $3d^3$  with other configurations, but fortunately the latter involve such high energies that the resulting modifications are probably not important.

#### THE $LS$ SYSTEM OF REPRESENTATION

One way of finding the necessary matrix elements would doubtless be to use Kramers'<sup>3</sup> symbolic  $\xi\eta$  method, closely related to group theory. For our purpose, however, it is simpler and more straightforward to utilize explicit wave functions. Some of the wave functions appropriate to Russell-Saunders coupling for the configurations  $d^3$  have been given by Condon and Shortley,<sup>4</sup> and the rest can be obtained by a procedure fully described by them.

These characteristic functions, of  $\mathcal{L}^2$ ,  $\mathcal{S}^2$ ,  $\mathcal{L}_z$  and  $\mathcal{S}_z$ , are as follows, omitting the quartet states and those doublet states given by Condon and Shortley:

$$\begin{aligned}
 ({}^2H\ 1) &= [8\beta + 6\theta + 4P - 3V - R + 3X - 2Z - \zeta]/(210)^{\frac{1}{2}}, \\
 ({}^2H\ 0) &= [\lambda + \gamma + 4Y - 2\alpha - 2\eta - W + 2Q - S]/(42)^{\frac{1}{2}}, \\
 ({}^2G\ 1) &= [12\beta - 6\theta + 6P + 6R - 12V - 3X + 7Z - 4\zeta]/(840)^{\frac{1}{2}}, \\
 ({}^2G\ 0) &= [\lambda - \gamma + 2\alpha - 2\eta - 2W + 2S]/(28)^{\frac{1}{2}}, \\
 ({}^2F\ 1) &= [4\beta + 6\theta - 6P + 2R + 4V - X + Z]/(120)^{\frac{1}{2}}, \\
 ({}^2F\ 0) &= [-\lambda - \gamma + 4Y - 2\alpha - 2\eta + 2W - 4Q + 2S]/(60)^{\frac{1}{2}}, \\
 (a\ {}^2D\ 1) &= [\beta - \theta + V - R]/2, \quad (a\ {}^2D\ 0) = [\alpha - \eta + W - S]/2, \\
 (b\ {}^2D\ 1) &= [-\beta - 3\theta - 4P + V + 3R + 2X - 2\zeta]/(84)^{\frac{1}{2}}, \\
 (b\ {}^2D\ 0) &= [-2\lambda + 2\gamma + 3\alpha - 3\eta - 3W + 3S]/(84)^{\frac{1}{2}}, \\
 ({}^2P\ 1) &= [-9\beta + 9\theta + 6P + 6V - 12R + X + 4Z - 5\zeta]/(630)^{\frac{1}{2}}, \\
 ({}^2P\ 0) &= [-3\lambda - 3\gamma + 2Y - \alpha - \eta - 4W + 8Q - 4S]/(210)^{\frac{1}{2}}.
 \end{aligned}$$

The value of  $M_L$  is indicated by the last index on the left side (0 or 1) and we have supposed in each

<sup>2</sup> W. G. Penney and R. Schlapp, *Phys. Rev.* **41**, 194 (1932); Schlapp and Penney, *ibid.* **42**, 666 (1932).

<sup>3</sup> H. A. Kramers, *Proc. Amst. Acad.* **33**, 953 (1930); **34**, 965 (1931).

<sup>4</sup> E. U. Condon and G. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 226.

instance that  $M_S = +\frac{1}{2}$ . We have used the abbreviations:

$$\begin{aligned}
 P &= (2^+1^-2^+), & Q &= (2^+0^-2^+), & R &= (2^+1^+2^-), & S &= (2^+0^+2^-), & V &= (2^-1^+2^+), \\
 W &= (2^-0^+2^+), & X &= (2^+0^-1^+)\sqrt{6}, & Y &= (1^+0^-1^+), & Z &= (2^+0^+1^-)\sqrt{6}, & \alpha &= (1^+0^+1^-), \\
 \beta &= (1^+1^-1^+), & \gamma &= (2^+-1^-1^+)\sqrt{6}, & \zeta &= (2^-0^+1^+)\sqrt{6}, & \eta &= (1^-0^+1^+), & \theta &= (1^+0^-0^+), \\
 \lambda &= (1^+1^-2^+)\sqrt{6},
 \end{aligned}$$

where a notation such as  $(0^+-2^-2^+)$  means an antisymmetrical wave function in which one electron has  $m_l=0$ , another has  $m_l=-2$ , and, the third has  $m_l=+2$ . The superscripts refer to the two spin possibilities  $M_S = \pm\frac{1}{2}$ . The electrons of course all have  $l=2$ , since the configuration is  $d^3$ . To get  $\psi(-M_L)$ , we reverse the sign of all the  $m_l$ , and multiply by  $(-1)^{M_L}$ , and to obtain states for  $M_S = -\frac{1}{2}$  we reverse the sign of all the superscripts.

Since the potential is of the form  $\Sigma V_i$ , its matrix components are simply expressible in terms of those of a single electron. The diagonal elements are

$$(a_1 \cdots a_n | V | a_1 \cdots a_n) = \sum_{i=1, \dots, N} (a_i | V_i | a_i).$$

The only other nonvanishing elements are of the form

$$(a_1 \cdots a_k \cdots a_n | V | a_1' \cdots a_l' \cdots a_n') = \epsilon(a_k | V | a_l')$$

with  $a_1' \cdots a_{l-1}' a_{l+1}' \cdots a_n'$  restricted to be merely a permutation of  $a_1 \cdots a_{k-1} a_{k+1} \cdots a_n$ . The factor  $\epsilon$  is  $+1$  or  $-1$  according as this permutation is even or odd. Since we are dealing with a three-electron system, the value of  $N$  is 3.

For the matrix  $(m_l | V_i | m_l')$  we have<sup>2</sup>

$$(m_l | V | m_l') = \frac{1}{2} \left\{ \frac{1}{6} (35m_l^4 - 155m_l^2 + 72) \delta_{m_l, m_l'} + 10\delta_{m_l, m_l'+4} + 10\delta_{m_l, m_l'-4} \right\} Dq, \tag{2}$$

where  $m_l, m_l' = -2, -1 \cdots +2$ , and where  $Dq$  is the constant of Penney and Schlapp,<sup>2</sup> viz.

$$2(m_l | r^4 | m_l) / 105.$$

### THE $L\Gamma$ SYSTEM OF REPRESENTATION

Our functions represent eigenstates of  $\mathfrak{L}$  and  $\mathfrak{S}$ , but it is not necessary to diagonalize  $\mathfrak{J}$ , as we are neglecting spin-orbit coupling, which is subordinate in the solid state. On the other hand, it is advisable to use as basis functions those which diagonalize the potential (1) apart from elements non-diagonal in  $L$ . Such functions must be classified according to their cubic representation<sup>5</sup>  $\Gamma$  rather than according to  $M_L$ . In other words, they diagonalize  $\mathfrak{L}^2$  but not  $\mathfrak{L}_z$ . The secular equations associated with the passage from the  $M_L$  to the  $\Gamma$  systems of representation have been given by Penney and Schlapp up to  $L=4$  and the case  $L=5$  can be treated by similar methods. (In their first paper they considered  $J=4$  rather than  $L=4$ , but the mathematical structure is similar.)

The transformation matrix  $(L\Gamma | LM_L)$  can thus be calculated, and is shown in Table I.

The representations  $\Gamma_4$  and  $\Gamma_5$  are triply degenerate, and in each case two of their wave functions are obtained by using the two sign possibilities in the left side of Table I, while the third is found either in the central or in the right portion. Each doubly degenerate state  $\Gamma_3$  has one wave function in the central part and one on the right. There are two threefold states of the form  ${}^2H\Gamma_4$ , and they are distinguished by the indices  $\alpha$  and  $\beta$ .

<sup>5</sup> For explanation of the different cubic representations, see H. A. Bethe, *Ann. d. Physik* **3**, 133 (1929).

TABLE I.\*

$M_L =$	$\mp 5$	$\mp 1$	$\pm 3$	$+2$	$-2$	$+4$	$-4$	$0$
${}^2H\Gamma_5$	$\frac{1}{2}(30)^{\frac{1}{2}}$	$-\frac{1}{2}\sqrt{7}$	$-\frac{1}{2}\sqrt{6}$	${}^2H\Gamma_5$	$\frac{1}{2}\sqrt{2}$	${}^2H\Gamma_{4\alpha}$	$\frac{1}{2}a^{\frac{1}{2}}/\sqrt{6}$	$-\frac{1}{2}ba^{\frac{1}{2}}/\sqrt{5}$
${}^2H\Gamma_{4\alpha}$	$-\frac{1}{2}d^{\frac{1}{2}}$	$\frac{1}{2}ad^{\frac{1}{2}}/(10)^{\frac{1}{2}}$	$-\frac{1}{2}ed^{\frac{1}{2}}/\sqrt{5}$	${}^2H\Gamma_3$	$\frac{1}{2}\sqrt{2}$	${}^2H\Gamma_{4\beta}$	$\frac{1}{2}b^{\frac{1}{2}}/\sqrt{6}$	$\frac{1}{2}ab^{\frac{1}{2}}/\sqrt{5}$
${}^2H\Gamma_{4\beta}$	$-\frac{1}{2}c^{\frac{1}{2}}$	$\frac{1}{2}bc^{\frac{1}{2}}/(10)^{\frac{1}{2}}$	$\frac{1}{2}fc^{\frac{1}{2}}/\sqrt{5}$	${}^2G\Gamma_5$	$\frac{1}{2}\sqrt{2}$	${}^2H\Gamma_3$	$\frac{1}{2}\sqrt{2}$	$0$
${}^2G\Gamma_5$	$0$	$\frac{1}{2}\sqrt{2}$	$-\frac{1}{2}(14)^{\frac{1}{2}}$	${}^2G\Gamma_3$	$\frac{1}{2}\sqrt{2}$	${}^2G\Gamma_4$	$\frac{1}{2}\sqrt{2}$	$0$
${}^2G\Gamma_4$	$0$	$\frac{1}{2}(14)^{\frac{1}{2}}$	$\frac{1}{2}\sqrt{2}$	${}^2D\Gamma_5$	$\frac{1}{2}\sqrt{2}$	${}^2G\Gamma_3$	$(7/24)^{\frac{1}{2}}$	$-(5/12)^{\frac{1}{2}}$
${}^2F\Gamma_5$	$0$	$-\frac{1}{2}(10)^{\frac{1}{2}}$	$\frac{1}{2}\sqrt{6}$	${}^2D\Gamma_3$	$\frac{1}{2}\sqrt{2}$	${}^2G\Gamma_1$	$(5/24)^{\frac{1}{2}}$	$(7/12)^{\frac{1}{2}}$
${}^2F\Gamma_4$	$0$	$\frac{1}{2}\sqrt{6}$	$\frac{1}{2}(10)^{\frac{1}{2}}$	${}^2F\Gamma_5$	$\frac{1}{2}\sqrt{2}$	${}^2F\Gamma_4$	$0$	$1$
${}^2D\Gamma_5$	$0$	$1$	$0$	${}^2F\Gamma_2$	$\frac{1}{2}\sqrt{2}$	${}^2D\Gamma_3$	$0$	$1$
${}^2P\Gamma_4$	$0$	$1$	$0$			${}^2P\Gamma_4$	$0$	$1$

\* Here  $a = 6 + (21)^{\frac{1}{2}}$ ,  $b = 6 - (21)^{\frac{1}{2}}$ ,  $c = \frac{1}{16}[153 + 33(21)^{\frac{1}{2}}]$ ,  $d = \frac{1}{16}[153 - 33(21)^{\frac{1}{2}}]$ ,  $e = 19 + 4(21)^{\frac{1}{2}}$ ,  $f = 19 - 4(21)^{\frac{1}{2}}$ .

The elements of  $V$  in the  $L\Gamma$  representation, measured in multiples of  $Dq$ , are now found to be

${}^2H$	${}^2G$	${}^2F$	${}^2D_a$	${}^2D_b$	${}^2H$	${}^2H$	${}^2G$	${}^2F$	${}^2P$
-1.335	-1.605	-1.055	7.30	-1.595	2.61	0	6.17	1.73	0.588
	1.86	2.535	-2.935	3.84		-2.61	4.45	-0.635	4.98
		-0.335	5.775	2.525			-1	-1.73	-2.78
	( ${}^2\Gamma_5$ )		-2	2.18		( ${}^2\Gamma_4$ )		1	-5.88
				1.81					0
${}^2H$	${}^2G$	${}^2D_a$	${}^2D_b$						
2	9.64	5.48	-1.195						( ${}^2F\Gamma_2   V   {}^2F\Gamma_2$ ) = -2
	-0.285	5.86	-7.66		${}^4F$	${}^4P$			( ${}^2G\Gamma_1   V   {}^2G\Gamma_1$ ) = -2
( ${}^2\Gamma_3$ )		3	-3.27		6	4			( ${}^4F\Gamma_5   V   {}^4F\Gamma_5$ ) = -2
			-2.715		( ${}^4\Gamma_4$ )	0			( ${}^4F\Gamma_2   V   {}^4F\Gamma_2$ ) = -12

These of course include elements nondiagonal in  $L$  as well as those elements which blend together the two  $D$  states. Only states corresponding to the same cubic representation and same multiplicity combine. Since the determinants are symmetrical, we omit writing the elements below the diagonal. The Dirac notation has been used for the representations occurring only once, whose elements are, of course, entirely diagonal.

To the matrix of the crystalline potential it is now necessary to add the matrix of the Russell-Saunders energy  $E$  of the free ion. The matrix elements for the states occurring once are all diagonal in the  $L\Gamma$  system of representation and are as follows expressed in wave number units measured upward from the ground state<sup>6</sup>

$${}^4F = 0, \quad {}^4P = 14,200, \quad {}^2G = 15,200, \quad {}^2P = 19,400, \quad {}^2H = 21,200, \quad {}^2F = (33,700) \text{ cm}^{-1}. \quad (3)$$

The elements corresponding to the two  $D$  states are

$$({}^2D_a | E | {}^2D_a) = 27,500, \quad ({}^2D_a | E | {}^2D_b) = 12,700, \quad ({}^2D_b | E | {}^2D_b) = 46,600 \text{ cm}^{-1} \quad (4)$$

with characteristic values

$${}^2D = 20,600, \quad {}^2D' = (53,500) \text{ cm}^{-1}. \quad (5)$$

<sup>6</sup> For spectroscopic data on the free Cr IV ion, see I. S. Bowen, Phys. Rev. 52, 1153, (1937). The writers are much indebted to Professor Bowen for communicating to them his determinations of the positions of the  ${}^2P$  and low  ${}^2D$  terms, which he has not published, but which we have incorporated in (3) and (5).

Entries in parenthesis mean that a direct spectroscopic determination is not available, and that the levels have been located approximately by extrapolation from isoelectronic configurations or by means of the "FG" relations of Slater-Condon-Shortley.

There are two useful checks which we have used against numerical errors in writing down the various preceding matrices. In the first place, the elements of the crystalline potential down the principal diagonal correspond to the conventional Penney-Schlapp theory,<sup>2</sup> and can be obtained, as they show, in a purely algebraic fashion independent of wave functions, by using essentially the methods of group theory. The latter does not determine a proportionality constant, but this can be obtained by using the Goudsmit<sup>7</sup> method of diagonal sums.<sup>6</sup> (The two <sup>2</sup>D states cannot, however, be resolved by this method.) In the second place, when all the Russell-Saunders energies are arbitrarily taken equal, i.e., (3) and (4) omitted, the *L* quantization becomes extraneous, and the electrons are individually quantized in the cubic field. Under these circumstances, the energy of an individual electron is  $-4Dq$  or  $6Dq$ , since solution of the characteristic value problem connected with (2) yields roots  $-4Dq$  and  $6Dq$ , occurring three and two times, respectively. Hence the roots of the related secular equation must in this other limiting case be of the form  $n \cdot (-4Dq) + (3-n) \cdot 6Dq$  ( $n=1,2,3$ ). An interesting but somewhat involved argument based on group theory and explained below in fine print, shows that the correlation of the different roots with the various secular equations is as follows for the doublet levels, in multiples of  $Dq$ :

$$\Gamma_1: -2; \quad \Gamma_2: -2; \quad \Gamma_3: -12, -2, -2, +18; \quad \Gamma_4: -12, -2, -2, 8, 8; \quad \Gamma_5: -12, -2, -2, 8, 8. \quad (6)$$

If we regard the diagonal elements of the determinants as known, from the conventional Penney-Schlapp theory or otherwise, then when the secular determinants are quadratics, the off-diagonal elements can be determined without the use of explicit wave functions by the Goudsmit inspection method,<sup>7</sup> i.e., simply by the requirement that the roots reduce properly to (6) in the corresponding limit. In particular, the formulas for the quartets can be obtained entirely by this inspection method, and we have consequently not bothered to write out the wave functions for them.

*Proof of (6).* When the Russell-Saunders energies are all taken equal, the electrons can be separately quantized in the crystalline field, and the wave functions considered to be simple products,<sup>8</sup> rather than sums of products of the individual functions as previously. The individual factors are characteristic functions of the "one-electron" secular problem connected with (2), and correspond to  $\Gamma_3$  or  $\Gamma_5$  of the cubic group, for these are the cubic resolution of the representation  $l=2$  of the rotation group. To apportion roots to the secular equations associated with the three-electron problem, we must evaluate the irreducible representations contained in the triple direct product. The theory of characters shows that

$$\begin{aligned} \Gamma_3 \times \Gamma_3 \times \Gamma_3 &= [\Gamma_1 + \Gamma_2 + \Gamma_3] + 2\Gamma_3, & \Gamma_5 \times \Gamma_5 \times \Gamma_5 &= [\Gamma_1 + \Gamma_4 + 2\Gamma_5] + (\Gamma_2) + 2\Gamma_3 + 2\Gamma_4 + 2\Gamma_6, \\ \Gamma_3 \times \Gamma_3 \times \Gamma_5 + \Gamma_3 \times \Gamma_5 \times \Gamma_3 + \Gamma_5 \times \Gamma_3 \times \Gamma_3 &= [\Gamma_4 + 2\Gamma_5] + (\Gamma_4) + 4\Gamma_4 + 4\Gamma_6, & (7) \\ \Gamma_3 \times \Gamma_5 \times \Gamma_5 + \Gamma_5 \times \Gamma_3 \times \Gamma_5 + \Gamma_5 \times \Gamma_5 \times \Gamma_3 &= [\Gamma_1 + \Gamma_2 + 2\Gamma_3 + \Gamma_4 + \Gamma_5] + (\Gamma_4 + \Gamma_5) + 2\Gamma_1 + 2\Gamma_2 + 4\Gamma_3 + 4\Gamma_4 + 4\Gamma_5. \end{aligned}$$

Here we have included in square and round parentheses the parts of the total direct product which are absorbed by the symmetrical and antisymmetrical direct products, respectively. The symmetrical product corresponds to an orbital wave function symmetrical in three electrons, and so is not allowed by the exclusion principle, while the antisymmetrical product obviously embodies the quartet states. The portion not enclosed in either type of parenthesis represents an intermediate type of symmetry appropriate to doublet states. The occurrence of these states is just half as great as that indicated by (7), because two states of this intermediate orbital symmetry are required in order to construct one totally antisymmetric wave function when the spin is included.<sup>9</sup>

The result (6) then follows from (7) on noting that a factor  $\Gamma_5$  or  $\Gamma_3$  on the left side of (7) corresponds, respectively, to an energy  $-4Dq$  and  $6Dq$  for a single electron. (We must correlate  $-4Dq$ ,  $6Dq$  with  $\Gamma_5$ ,  $\Gamma_3$  rather than vice versa, because triple and double roots of the secular problem connected with (2) must correspond to three- and twofold representations, respectively.)

The derivation of (7) itself requires some discussion, which we now give. The reduction of the total direct product is obtained by standard methods of group theory. The symmetrical direct product of the form  $a \times a \times a$  can be reduced by

<sup>7</sup> S. Goudsmit, Phys. Rev. **31**, 946 (1928); **35**, 1325 (1930).

<sup>8</sup> The wave function is, of course, expressible as a simple product only before "antisymmetrization" with respect to spin and orbit combined. Our classification of symmetry types in the section in fine print relates to purely orbital permutation, and of course only an antisymmetrical representation is allowed when spin is included.

<sup>9</sup> Cf. E. Wigner, Zeits. f. Physik **40**, 492 (1927); *Gruppentheorie*, Chap. XXII.

rules given by Tisza.<sup>10</sup> There is no antisymmetrical portion involved in  $\Gamma_3 \times \Gamma_3 \times \Gamma_3$ , since an antisymmetric triple product cannot be constructed when only two functions are available, as is the case for a doubly degenerate representation like  $\Gamma_3$ . With  $\Gamma_3$  there are three functions available, so that one antisymmetrical product can be built. This must correspond to a onefold representation. Hence  $\Gamma_2$  represents the antisymmetrical part of  $\Gamma_3 \times \Gamma_3 \times \Gamma_3$ , inasmuch as  $\Gamma_1$ , the only other onefold representation contained in the total direct product, has already been absorbed by the symmetrical portion. To find the symmetrical and antisymmetrical parts of  $[a \times a] \times b$  we use the following rule: If a given representation occurs  $n$  times in  $[a \times a] \times b$ , it is contained  $n$  times in the symmetrical or antisymmetrical parts of  $[a \times a] \times b + [a \times b \times a] + [b \times a \times a]$  according as it arises from  $[a \times a]_{\text{sym}} \times b$  or  $[a \times a]_{\text{anti}} \times b$ . This statement follows from the fact that one symmetrical or antisymmetrical wave function can be built from a triple product if two factors are already symmetrized or antisymmetrized, and the third is unlike the other two.

## RESULTS

To evaluate the roots of our secular determinants numerically, we take the constant  $Dq$  equal to  $1500 \text{ cm}^{-1}$ , as this is the round value indicated by susceptibility data.<sup>11,12</sup> The levels in solid chrome alum then prove to be

${}^2\Gamma_5$ 76,500 $\text{cm}^{-1}$	${}^2\Gamma_4$ 47,500 $\text{cm}^{-1}$	${}^2\Gamma_5$ 25,900 $\text{cm}^{-1}$
${}^2\Gamma_3$ 75,600	${}^2\Gamma_4$ 40,500	${}^4\Gamma_4$ 23,100
${}^2\Gamma_4$ 59,000	${}^2\Gamma_3$ 36,400	${}^2\Gamma_4$ 19,300
${}^2\Gamma_3$ 55,900	${}^4\Gamma_4$ 36,100	${}^2\Gamma_3$ 18,200
${}^2\Gamma_5$ 48,700	${}^2\Gamma_5$ 34,600	${}^4F\Gamma_5$ 15,000
${}^2\Gamma_5$ 48,700 <sup>12</sup>	${}^2\Gamma_4$ 34,400	${}^4F\Gamma_2$ 0.
${}^2\Gamma_2$ 48,600	${}^2\Gamma_1$ 30,200	

Here the origin is taken at the ground state in the solid state, which is depressed  $12Dq = 18,000 \text{ cm}^{-1}$  as compared with the ground state of the free ion. The corresponding levels for the free  $\text{Cr}^{+++}$  ion, which are basic to the calculation, are given in (3) and (5).

According to (8) the lowest doublet level is  $18,200 \text{ cm}^{-1}$  above the ground state. Our interpretation<sup>13</sup> of Spedding and Nutting's measurements<sup>14</sup> on the Zeeman effect requires that there be doublet levels only  $14,900 \text{ cm}^{-1}$  above the basic term. The discrepancy of about  $3000 \text{ cm}^{-1}$  probably seems rather large to atomic spectroscopists accustomed to specifying an energy level to within less than a wave number. However, the agreement seems adequate when it is remembered

<sup>10</sup> L. Tisza, *Zeits. f. Physik* **82**, 48 (1933).

<sup>11</sup> Cf. reference 2 and J. H. Van Vleck, *J. Chem. Phys.* **7**, 81 (1939).

<sup>12</sup> The entry 48,700 appears twice because there is approximately a double root of the  ${}^2\Gamma_5$  secular equation at this position.

<sup>13</sup> J. H. Van Vleck, *J. Chem. Phys.* **8**, 790 (1940).

<sup>14</sup> F. H. Spedding and G. C. Nutting, *J. Chem. Phys.* **3**, 369 (1935).

that calculations on the solid state are necessarily more or less qualitative and lack the precision of the refined theory of the spectra of free atoms. It is to be emphasized that we are making a somewhat different application than usual of the theory of the crystalline potential, as we are using the latter to locate the position of excited levels rather than merely to determine the magnetic susceptibility of the ground state. The rough accord achieved with experiment by our calculations can be regarded both as a confirmation of our interpretation of Spedding and Nutting's data, and of the real physical significance of the constant  $Dq$  of the Penney-Schlapp cubic crystalline potential. The discrepancy may be due to the fact that our assumed value  $1500 \text{ cm}^{-1}$  of  $Dq$ , although correct as regards rough order of magnitude, may be a little low. There are no adequate determinations of  $Dq$  available for chrome alum, and it is necessary for us to base our estimates on salts not merely of different chemical composition, but also of different valence.<sup>15</sup> The best measurements of  $Dq$  are furnished by susceptibility data on Tutton or other closely related salts of nickel. The doublets are brought to within the proper distance  $14,900 \text{ cm}^{-1}$  of the basic quartet if we take  $Dq$  about  $1820 \text{ cm}^{-1}$ , and such a change

<sup>15</sup> It is hard to tell whether  $Dq$  should increase or decrease in going from nickel to chromium, as the trivalent rather than divalent behavior tends to diminish the mean value of  $x^4 + y^4 + z^4$ , whereas the lesser nuclear charge acts in the opposite direction. Furthermore, changes in  $x^4 + y^4 + z^4$  may be more than compensated by corresponding alterations in the distance  $R$  to the nearest water molecules, since increasing valence diminishes  $R$ , and since  $Dq$  is proportional to  $R^{-5}$  or  $R^{-6}$  according as the molecules act as point charges or as dipoles. The observations of  $Dq$  directly for chromium salts by Janes and others are not made on alums, and are not reliable, since determinations of  $Dq$  in chromium from susceptibility measurements are inordinately difficult because they require the precise determination of a very small deviation of the susceptibility from the "spin only" value. Cf. reference 11.

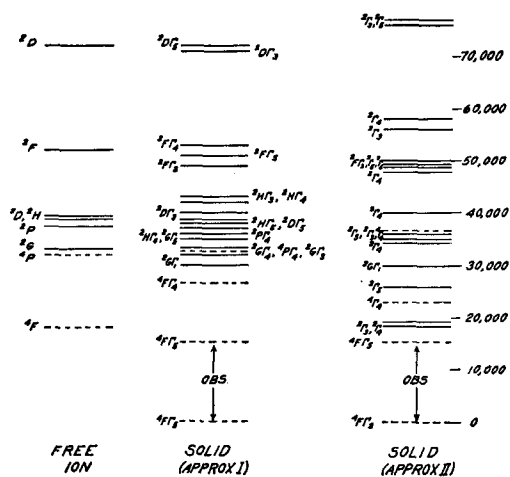


FIG. 1. The left side of the figure gives the empirical energy levels for the free ion, while approximations I and II show the corresponding positions in the solid alum, and are, respectively, exclusive and inclusive of matrix elements nondiagonal in the quantum number  $L$ . Doublet states are indicated by solid lines, and quartets by dashed. The preceding paper shows that the "observed" discrete absorption represents intersystem combination. Hence to obtain agreement with experiment, a solid line should coincide with the upper end of the arrow.

in the value of  $Dq$  does not seem excessive in view of the elements of uncertainty just mentioned. Quite irrespective of the question of the size of  $Dq$ , there are other errors latent in the calculations which are sufficient to explain the discrepancy. The field is, in the first place, not accurately cubic, and furthermore the "one-atom" method envisaged by the use of a crystalline potential is itself only an approximation.<sup>16</sup> Actually in the solid state one has all the intricacies of the "many-atom" problem, in particular the complications due to the Jahn-Teller effect, as previously discussed by one of the authors,<sup>16</sup> and also possible overflowing of the electrons onto adjacent atoms,—an effect recognized in the method of molecular orbitals but not in that of crystalline potentials.

One thing stands out clearly from the calculations, and that is that in the case of the doublet states it is very essential to include the effect of the matrix elements nondiagonal in  $L$ . In fact, without them, the deepest doublet level would be a  ${}^2G\Gamma_1$  term  $30,200\text{ cm}^{-1}$  above the ground state, far too high. It was our perplexity at this disagreement that led us to undertake

<sup>16</sup> For further discussion see, for instance, J. H. Van Vleck, *J. Chem. Phys.* **7**, 61 (1939).

the detailed calculations of the present paper inclusive of nondiagonal elements in  $L$ . The blending of various doublet states caused by the nondiagonal elements in  $L$  is so complete that the quantum number  $L$  usually loses all meaning, and it is impossible to classify the levels as  ${}^2G$ ,  ${}^2H$ , etc. (except for the representations  $\Gamma_1$ ,  $\Gamma_2$  involving only one value of  $L$ ). Spedding and Nutting<sup>14</sup> have already suggested that the calculation would probably yield this result. For the quartets, however, the error involved in dropping nondiagonal terms in  $L$  is not serious. Without the diagonal terms, the  ${}^4F\Gamma_4$  and  ${}^4P\Gamma_4$  states would fall at  $27,000$  and  $32,200\text{ cm}^{-1}$  instead of  $23,100$  and  $36,100\text{ cm}^{-1}$ , respectively.

The results of our calculations are shown graphically in Fig. 1, where approximations I and II are, respectively, exclusive and inclusive of the nondiagonal elements in  $L$ . The bottom level in approximation I is considerably deeper than that for the free ion because the ground state  ${}^4F\Gamma_2$  is depressed  $12Dq=18,000\text{ cm}^{-1}$  by the crystalline potential. There is no commensurate depression of the doublet states unless we include nondiagonal elements in  $L$ , and it is for this reason that with Russell-Saunders coupling the doublet-quartet interval turns out to be  $30,200\text{ cm}^{-1}$  even though the line  ${}^4F-{}^2G$  falls at  $15,200\text{ cm}^{-1}$  in the free ion. It will be noted that there is little correspondence between the energy levels of the solid and gas, and theories<sup>17</sup> of the solid state based on the assumption that the displacement between the solid and gaseous state amounts to only a few hundred  $\text{cm}^{-1}$  are obviously spurious.

It will be noted that according to our computations the  ${}^4F\Gamma_5$  state is not far removed from the upper states studied by Spedding and Nutting. The Zeeman pattern resulting from the transition  ${}^4F\Gamma_2-{}^4F\Gamma_5$  would be quite different from that of the observed lines, as stressed in the preceding paper.<sup>13</sup> One wonders why the line  ${}^4F\Gamma_2-{}^4F\Gamma_5$  has escaped observation. The answer is, no doubt, that all the excited levels are somewhat lower than shown in the figure, since otherwise the  ${}^2T_3$  state does not fall at the right position and that consequently the quartet is displaced down to a region where it is masked

<sup>17</sup> E.g. O. Deutschbein, *Zeits. f. Physik* **77**, 489 (1932); D. M. Bose and S. Datta, *Zeits. f. Physik* **80**, 376 (1933).



by the continuum associated with transitions of exterior ( $4s$ ,  $4p$ , etc.) rather than  $d^3$  electrons. This continuum has a rift merely between about 14,000 and 16,000  $\text{cm}^{-1}$ .<sup>18</sup> The narrowness of this gap makes it impossible to try to observe most of the levels shown in Fig. 1. Spedding and Nutting have observed several levels in the narrow region accessible to observation, but it would be futile to try to identify them with the individual roots of our secular determinant. In the first place, degenerate cubic states will be split by the noncubic portions of the crystalline field, and besides this, some of the states may be repeated at intervals of the order 10 to 10<sup>2</sup>  $\text{cm}^{-1}$  due to vibrational structure. Hence the various levels found experimentally are not necessarily to be identified with different electronic states.

#### STATES OF HIGHEST MULTIPLICITY IN VANADIUM, COBALT, AND NICKEL

Because of the reciprocal character of the configurations  $d^3$  and  $d^7$  our calculations also apply to  $\text{Co}^{++}$ , with merely a change in sign of the constant  $Dq$ . It can be shown<sup>19</sup> that the determinants for the quartets also apply to the

<sup>18</sup> There is also a rift in the vicinity of 22,000  $\text{cm}^{-1}$ , and sharp lines are also observed in this vicinity (cf. F. H. Spedding and G. C. Nutting, *J. Chem. Phys.* **2**, 421, 1934). Reference to our table of calculated levels for the solid shows that these lines probably arise from  ${}^2\Gamma_6$  or  ${}^4\Gamma_4$  upper states, when allowance is made for the fact that our computed positions of excited levels are probably 3000  $\text{cm}^{-1}$  or so too high. It would be interesting if Zeeman observations were available on these lines, for the preceding paper (reference 13) shows that the behavior of the Zeeman patterns would be quite different according as the lines are doublets or quartets.

<sup>19</sup> There is a reciprocal relation between the behavior of the triplet states of  $d^3$  (or  $d^7$ ) and the quartet levels of  $d^4$  (or  $d^6$ ), for the filled states in the latter can be correlated with "holes" in the Stark pattern of the former inasmuch as a  $d$  level has five spatial substates. There is, however, a sign reversal in  $Dq$  when one goes from one case to the other. See J. H. Van Vleck, *Phys. Rev.* **41**, 208 (1932).

corresponding triplets in  $\text{V}^{+++}(d^2)$  and  $\text{Ni}^{++}(d^8)$  with a sign change in  $Dq$  for  $\text{V}^{+++}$ , but not for  $\text{Ni}^{++}$ , as in the latter there are two compensating sign changes. These observations enable one to study how far the susceptibility calculations for vanadium and cobalt are modified by the partial loss of significance of the quantum number  $L$  as suggested by Spedding. In the case of chromium, this question does not enter, as the ground state is the only one belonging to the representation  ${}^3\Gamma_2$ . In vanadium the interval  ${}^3F-{}^3P$  for the free ion is 13,000  $\text{cm}^{-1}$ , and we find on solving our secular equation for  ${}^3\Gamma_4$  states, that the basic state  ${}^3F\Gamma_4$  is of the form

$$\psi = (0.94)^{\frac{1}{2}}({}^3F) - (0.06)^{\frac{1}{2}}({}^3P). \quad (8)$$

This result was quoted in a previous paper by one of the writers and shows that in Siegert's calculations, the assumption of Russell-Saunders coupling is much closer to the truth than that of complete breakdown.<sup>20</sup> In the case of  $\text{Co}^{++}$  the interval  ${}^3F-{}^3P$  is somewhat wider than in  $\text{V}^{+++}$ , and the coefficients are about  $(0.95)^{\frac{1}{2}} - (0.05)^{\frac{1}{2}}$ . The "contamination" by  ${}^4P$  is too small to alter materially.<sup>21</sup> Schlapp and Penney's calculation of the susceptibility of cobaltous compounds made on the assumption that the basic state is pure  ${}^4F$ .

<sup>20</sup> The results mentioned in fine print on p. 69 of a previous paper, reference 1, follow from the fact that the departures from Russell-Saunders coupling reduce the orbital moment of the  ${}^3F\Gamma_4$  state by a factor  $a^2 - \frac{2}{3}b^2$  as compared with ideal R-S coupling, where  $a$  and  $b$  are, respectively, the first and second coefficients in (8). The values of  $a^2$  and  $b^2$  corresponding to complete breakdown of this coupling (i.e., individual quantization) would be  $\frac{4}{3}$ ,  $\frac{1}{3}$ .

<sup>21</sup> The incipient breakdown of the Russell-Saunders coupling lowers the orbital moment matrix for the  ${}^4F\Gamma_4$  state of cobalt by about 8 percent, and so perhaps reduces by about 16 percent the deviations of the calculated susceptibility of cobalt from the spin only value, since the susceptibility involves the magneton number quadratically. (Exact, reliable figures cannot, however, be given without long calculations, which do not seem worth while.) This change is in the right direction, but not large enough.