' Weak-field ' Ligand-field Calculation for Tetragonally Distorted d^2 and d^8 Systems

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The d^2 and d^8 crystal-field calculation of Ballhausen and Liehr has been extended to include tetragonal distortion, Trees correction, and all off-diagonal spin–orbit coupling and crystal-field matrix elements. Parameters used are evaluated and a minimum set selected. Those features of the calculation capable of experimental verification and use are emphasised. The calculation is used to predict as accurately as possible the spectra of tetragonally distorted nickel(II) systems.

VISIBLE and near i.r. spectra of transition-metal complexes contain considerable information of use to the chemist with regard to structure and electronic properties, and yet surprisingly little is really understood about the nature of the spectra. The best assessment of the relative-energy positions is still given by ligand-field theory, and the small separation between levels and the difficulties of a good open-shell molecular orbital calculation suggest that, for the time being at least, this will remain the case. At the present time, understanding of the theory and its limitations is far from satisfactory, and the calculation for d^2 and d^8 systems reported in this paper is intended to help in this respect.

Smith *et al.*[1] and Weakliem[2] have attempted to analyse spectra of tetrahedral nickel(II) ions, using the strong-field approach. There is considerable disparity between these results and the method of approach has been criticised by Ferguson.[3] The best weak-field analysis to date is that of Liehr and Ballhausen,[4] but their calculation does not include any low-symmetry field perturbation and so precludes an assessment of the many non-cubic complexes. Ferguson[3] demonstrated the accuracy of the cubic calculation by assigning Ni^{2+} spectra in $KMgF_3$, and Couch and Smith[5] obtained good fits to Ni^{2+} spectra in Cs_3MgCl_5 using a calculation involving the low-symmetry field perturbation. König[6] has collected much of the accurate spectroscopic data available for 3*d* transition-metal ions, but he has not used a complete calculation to analyse these data.

Full exploitation of the symmetry properties of molecules has contributed to much of the success of ligand-field theory. These properties can be used to best advantage in cubic systems where only one radial parameter (*Dq*) is necessary. However, on lowering the symmetry of the system, the number of radial parameters increases as the advantage of symmetry is reduced. Thus, there is the risk of ' over-parametrising ' if we attempt to apply ligand-field theory to molecules of very low symmetry. For an analysis of electronic spectra of the many non-cubic complexes, it appears to us that maximum advantage is gained by applying a tetragonal or trigonal perturbation to the cubic system.

Two particularly noticeable features of the calculation

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[1] G. P. Smith, C. H. Liu, and T. R. Griffiths, *J. Amer. Chem. Soc.*, 1964, **86**, 4796.

[2] H. A. Weakliem, *J. Chem. Phys.*, 1962, **36**, 2117.

[3] J. Ferguson, *Progr. Inorg. Chem.*, 1970, **12**, 159.

[4] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (*New York*), 1959, **6**, 174.

[5] T. W. Couch and G. P. Smith, *J. Chem. Phys.*, 1970, **53**, 1336.

[6] E. König, *Structure and Bonding*, 1971, **9**, 175.

which could be verified experimentally are the splittings under low-symmetry fields of the tetrahedral ${}^3T_1(F) \longrightarrow {}^3T_2(F)$ transition, and the overall width of, and splittings within, the ${}^1G$ manifold. The former of these has been demonstrated by Goodgame.[7] Transitions to excited states arising from the ${}^1G$ free-ion term have been largely neglected.

In this paper we make an appraisal of the ligand-field method, as applied to tetrahedral nickel(II) systems, using a fairly complete calculation, neglecting only small perturbations such as spin–spin interaction. We point out the various transitions of the spectra which are sensitive to particular perturbations, and have assessed the effect of each of the parameters to arrive at a minimum set for which an accurate fit would be expected. The conclusions we draw, with the exception of remarks concerning the Trees correction,[8] which strictly refers to Ni^{2+}, are general for tetragonally distorted d^2 and d^8 systems. It is impossible to present sufficient data graphically to represent every possible case, so that we publish in the Appendix a list of the necessary matrix elements required to perform the calculation on other systems.

The Proposed Model.—We have concentrated on the d^8 situation in which Ni^{2+} is at the centre of a tetrahedron of ligands which can be elongated along the S_4 axis to lower the symmetry to D_{2d}. The Hamiltonian used is that in equation (1), where H_0 refers to the

$$H = H_0 + \frac{e^2}{r_{12}} + \sum_{i=1,2} \xi(r_i) l_i s_i + V_{\text{tetrahedral}} + V_{\text{tetragonal}} + l_1 l_2 \qquad (1)$$

Hamiltonian operator for hydrogen-like wave functions of the free ion. The first term in the expression is the interelectron repulsion term and we use the usual Racah parameters B and C. The second term is the spin–orbit coupling term and the matrix elements were of the form (2). The selection rules $\Delta L = 0 \pm 1$, $\Delta S = 0 \pm 1$,

$$\langle m_l^{m_s}\, m_{l'}^{m_s'} | \sum_{i=1}^{2} \xi l_i \,.\, s_i | m_l^{m_s}\, m_{l'}^{m_s'} \rangle \qquad (2)$$

$$\text{where} \quad \sum_{i=1}^{2} \xi l_i s_i = \zeta[l_{z1}s_{z1} + \tfrac{1}{2}(l_{+1}s_{-1} + l_{-1}s_{+1})] + \zeta[l_{z2}s_{z2} + \tfrac{1}{2}(l_{+2}s_{-2} + l_{-2}s_{+2})]$$

$\Delta J = 0$, and $\Delta M = 0$ were used to establish which matrix elements were required. A different parameter ζ is in theory required for each term and for each set of elements between pairs of terms. $V_{\text{tetrahedral}}$ and $V_{\text{tetragonal}}$ are the crystal-field terms.

Wave functions for the d^8 configuration (equivalent to two positive holes) were of the form $|LM_LSM_S\rangle$, from which normalised two-electron eigenfunctions $|m_l^{m_s} m_{l'}^{m_s'}\rangle$ were obtained using the lowering operators L_- and S_-. The matrix elements (3) were obtained by the method

$$\langle m_l^{m_s} m_{l'}^{m_s'} | V_{\text{tetrahedral}} + V_{\text{tetragonal}} | m_l^{m_s} m_{l'}^{m_s'} \rangle \qquad (3)$$

described by Ballhausen[9] in terms of the radial parameters Dq, D_S, and D_T. The last two parameters are defined by equation (4), where r is the distance from the

$$D_S = -\frac{2}{7} r^2 \left(\frac{1}{b^3} - \frac{1}{a^3}\right); \quad D_T = -\frac{2}{21} r^4 \left(\frac{1}{b^5} - \frac{1}{a^5}\right) \qquad (4)$$

electron to the nucleus and a and b are distances from the ligands to the nucleus. The diagonal perturbation $l_1 l_2$ (Trees correction α) was introduced to take some account of the orbit–orbit interaction. All off-diagonal elements within and between terms were calculated for each of the perturbations and the complete matrix diagonalised using a Jacobi routine.

Finally, we tested the calculation, excluding the low-symmetry field perturbation, by fitting spectra of Ni^{2+} in $KMgF_3$ already fitted accurately by Ferguson.[3] We obtained excellent agreement with his calculation.

RESULTS

We assess first the application of the calculation to free-ion spectra ($V_{\text{tetrahedral}} + V_{\text{tetragonal}}$ set equal to zero) measured by Shenstone.[10] Theoretical and observed values are tabulated in Table 1, from which it can be seen that a good fit to experiment is obtained for all the levels except ${}^1G$, using the parameters B, C, and ζ. The ${}^1G$ level is always badly predicted by theory, presumably due to configuration interaction.[2] If transitions from the centre of gravity of the ground term (${}^3F$) to that of the excited terms are considered, then we should be able to get an exact fit to experiment by introducing another parameter α (Trees correction). However, this procedure is not straightforward since the relative separations of the free-ion terms affects the off-diagonal spin–orbit matrix elements between them, and causes the spin–orbit components of each term to vary in a complex manner. By introducing a value of $\alpha = 90$ cm^{-1}, the best fit was obtained for all the free-ion levels. The greatest error was still in the ${}^1G$ level which is predicted 233 cm^{-1} above the experimental value (*cf.* 1466 cm^{-1} below the experimental value using $\alpha = 0$). Since we have found that levels arising from the ${}^1G$ free-ion term may be particularly useful as an indication of the degree of distortion in nickel(II) complexes, and we cannot sensibly discuss effects of changes in the ligand-field parameters when one of their major uses is to compensate for a dis-

TABLE 1

Free-ion levels of nickel(II)

Free-ion term	Observed energy/cm^{-1}	Calculated energy/cm^{-1}	
		a	*b*
${}^3F_4$	0	0	0
${}^3F_3$	1361	1352	1351
${}^3F_2$	2270	2265	2264
${}^1D_2$	14032	14031	14032
${}^3P_2$	16662	16723	16717
${}^3P_1$	16978	16983	16976
${}^3P_0$	17231	17241	17236
${}^1G_4$	23109	21663	23342

[a] $B = 1042$, $C = 4060$, $\xi = -668$, $\alpha = 0$ cm^{-1}. [b] $B = 1101{\cdot}6$, $C = 4183$, $\xi = -668$, $\alpha = 90$ cm^{-1}.

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[7] D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 1965, **4**, 139.

[8] R. E. Trees, *Phys. Rev.*, 1951, **82**, 683.

[9] C. J. Ballhausen, 'Introduction to Ligand Field Theory,' McGraw-Hill, New York, 1962, p. 99.

[10] A. G. Shenstone, *J. Opt. Soc. Amer.*, 1954, **44**, 749.

crepancy in the free-ion term, we have included the Trees correction in the rest of our calculation.

The interelectron repulsion integrals give rise to the Slater–Condon parameters F_2 and F_4, which are simply related to the Racah parameters B and C.[9] Parameters B and C are generally regarded as more convenient and we have used them in this case. Ferguson[3] has pointed out that the F_2 and F_4 integrals each have a different radial dependence, and F_2 should be more sensitive to changes in the nature of the ligand. It should therefore be possible to establish trends, in the values of F_2 and F_4 and the $F_2 : F_4$ ratio with changes in the ligands, which are more consistent than those using the parameters B and C. However, we were unsuccessful because insufficient spectral levels have been accurately assigned which are not subject to displacement by the Jahn–Teller effect. Specifically, an orbital singlet spin-forbidden level, *e.g.* the $B_2(^1D)$ level, must be found in a number of complexes before trends can be evaluated.

The problem with the spin–orbit coupling perturbation is the large number of parameters required for what is in fact a small perturbation. The usual practice is to set all ζ values equal to that chosen for the ground state. We investigated this. The ^3F levels should be most sensitive to effects involving matrix elements between terms, and values of these parameters from the free-ion value to that of zero were used. The major effect in changing from one extreme to the other was a rise in the energy levels of the ^3F by *ca.* 50 cm^{-1}. In no case was any reasonably large effect noted, so that all ζ values between terms were set equal to the value chosen for ^3F term. A similar result was obtained within terms so that we in fact used only one ζ parameter.

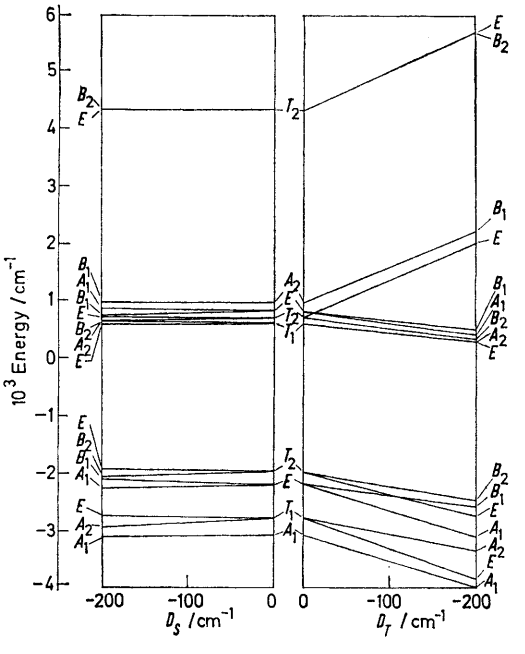

FIGURE 1 Variation of ^3F levels with the parameters D_S and D_T. $B = 740$, $C = 3680$, $Dq = 350$, and $\zeta = 560$ cm^{-1}

The approximate value of Dq is well known but we found that it was lowered by application of the low-symmetry field perturbation. The parameters D_S and D_T are not independent; they both depend on the ratio $a : b$, but the nature of the relation is complex so that we treat them here as independent. The value of D_T should be larger than that of D_S for small distortions.

The effect on the ^3F levels of increasing D_S and D_T is shown in Figure 1. The levels are insensitive to D_S and very sensitive to D_T. In the Figure tetrahedral spin–orbit assignments are shown in the centre and distorted assignments at the sides. The $^3T_1 \longrightarrow {}^3T_2$ transition is split by the low-symmetry field to a considerable extent, in agreement with experimental observations by Goodgame[7] and Weakliem[2] that this band is very broad. The ground state drops more quickly than the excited states with increasing distortion, so that the energies of the ^3F (and ^3P) peaks observed in the spectrum will be considerably higher than is usual in tetrahedral systems if a tetragonal distortion is present.

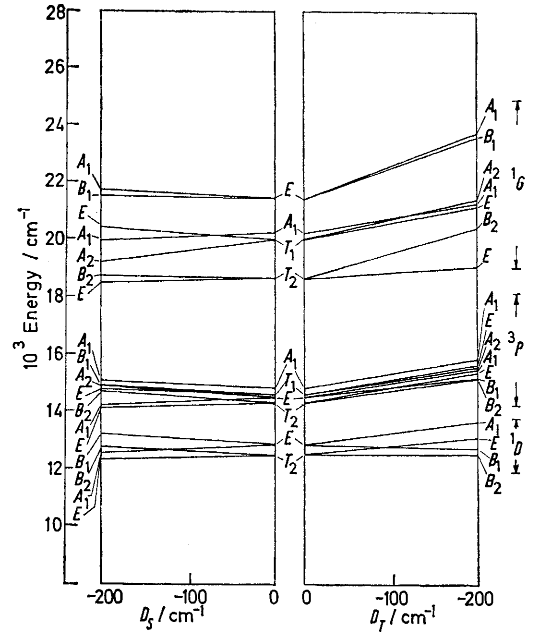

FIGURE 2 Variation of ^1G, ^3P, and ^1D levels with the parameters D_S and D_T. Other parameters as in Figure 1

Figure 2 shows D_S and D_T parameter variations in states arising from the other free-ion terms, neglecting the high-lying ^1S term. The parameter D_S causes the largest split in the band manifold of the ^3P levels. The actual separation is still too small to explain the bands observed in the usual ^3P spectra of tetrahedral nickel(II) ions. They are probably of vibrational–electronic origin, a statement borne out by the large drop in intensity of the high-energy part of the spectrum between room temperature and 4 K.

The ^1D and ^1G levels both show appreciable distortion effects. For example, the width of the ^1G band manifold increases with increasing D_T, and the relative positions of the lowest energy E and B_2 levels vary markedly. The ^1G bands lie in the visible region of the spectra and their sensitivity to distortion makes them a good probe of structure in nickel(II) complexes. There are few data available relating to these levels and we are investigating the spectra of the complexes $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$ which contain tetragonally distorted nickel(II) ions. Since the vibrational fine structure and temperature dependence of the bands requires a complex interpretation, this investigation will be published separately, but we have fitted the calculation to the main features of the spectra using the parameters Dq, D_T, B, C, α, and ζ. The spectra have sharp band edges at 4·2 K and we have chosen to fit these as representative of the approximate no-phonon positions of the bands. The agreement is shown in Table 2. Values obtained for the parameters B, C, α, and ζ are in reasonable agreement with those of previous work. The parameters Dq and D_T have not been sufficiently used in fitting tetragonally distorted spectra to make a real comparison with previous experiments possible. In Table 2, the highest B_1 level arising from the ^1G free-ion term is in error, particularly in one complex, but, since the only observation of this level has been in the complexes $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$, further work would be required before this discrepancy could definitely be ascribed to a failure in the calculation.

TABLE 2

Energies of *d*–*d* transitions of the ion nickel(II) in the complexes $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$

$(Et_4N)_2NiBr_4$ Energy/cm^{-1}			$(Et_4N)_2NiCl_4$ Energy/cm^{-1}	
Experimental	Calc.[a]	Symmetry designation	Experimental	Calc.[b]
6410	6401	$B_2(^3F)$	6944	7442
10400 [c]	10533	$B_2(^1D)$	11500 [c]	11678
10850 [c]	10710	$E(^1D)$	12150 [c]	11958
12877	12827	$E(^3P)$	13912	14076
16540	16543	$E(^1G)$	18198	18328
17483	17457	$B_2(^1G)$	19608	19610
17966	18121	$E(^1G)$	20408	20218
20550	18992	$B_1(^1G)$	21978	21291

[a] $B = 698$, $C = 2960$, $Dq = 187$, $D_T = -180$, $\zeta = -520$, $\alpha = 55$ cm^{-1}. [b] $B = 753$, $C = 3350$, $Dq = 200$, $D_T = -240$, $\zeta = -560$, $\alpha = 65$ cm^{-1}. [c] No-phonon lines estimated to an accuracy of ± 70 cm^{-1}.

CONCLUSIONS

The weakest feature of the calculation is the necessity to use four parameters B, C, α, and ζ to fit the free-ion terms of Ni^{2+}, but without all of them the ligand-field parameters will be distorted to take account of the resulting discrepancies.

For fairly small distortions, only two ligand-field parameters are of importance, Dq and D_T, since the value of D_S for small distortions is less than that of D_T and the levels are insensitive to D_S in any case. The value of Dq depends on the degree of tetragonal distortion so that its use, in any but strictly cubic systems, to indicate ligand-field strength could be misleading. Two major features of the effect of the low-symmetry field perturbation could be used to study distortion experimentally, *viz.* the marked splitting of the $^3T_1 \longrightarrow {}^3T_2(^3F)$ transition and the width of the manifold of ^1G levels.’

APPENDIX

The secular determinant is symmetrical across the leading diagonal so that the following condition for matrix elements $A(i,j)$ holds:

$$A(i,j) = A(j,i)$$

The matrix elements are as follows:

$$A(1,1) = A(9,9) = 2Dq + 12B + 2C + 4D_S - 2D_T + 20\alpha$$

$$A(1,5) = A(5,9) = 10Dq/70^{\frac{1}{2}}$$

$$A(1,10) = A(9,30) = \zeta$$

$$A(1,33) = A(9,33) = 20Dq/14^{\frac{1}{2}}$$

$$A(1,45) = A(9,45) = 20^{\frac{1}{2}}Dq$$

$$A(2,2) = A(8,8) = -3Dq + 12B + 2C + D_S + 3D_T + 20\alpha$$

$$A(2,6) = A(4,8) = 10Dq/28^{\frac{1}{2}}$$

$$A(2,13) = A(8,27) = A(11,13) = A(12,14) = A(26,28) = A(27,29) = 3^{\frac{1}{2}}\zeta/2$$

$$A(2,34) = A(8,32) = 10(6/28)^{\frac{1}{2}}Dq$$

$$A(3,3) = A(7,7) = -11Dq/7 + 12B + 2C - 8D_S/7 + 11D_T/7 + 20\alpha$$

$$A(3,7) = 15Dq/7$$

$$A(3,12) = A(7,28) = (1/28)^{\frac{1}{2}}\zeta$$

$$A(3,14) = A(7,26) = (3/7)^{\frac{1}{2}}\zeta$$

$$A(3,16) = A(4,17) = A(6,23) = A(7,24) = (15/28)^{\frac{1}{2}}\zeta$$

$$A(3,31) = A(7,35) = 30 \,.\, 3^{\frac{1}{2}}Dq/7 + 4 \,.\, 3^{\frac{1}{2}}D_S/7 - 30 \,.\, 3^{\frac{1}{2}}D_T/7$$

$$A(3,35) = A(7,31) = 10 \,.\, 3^{\frac{1}{2}}Dq/7$$

$$A(4,4) = A(6,6) = 9Dq/7 + 12B + 2C - 17D_S/7 - 9D_T/7 + 20\alpha$$

$$A(4,15) = A(6,25) = (3/28)^{\frac{1}{2}}\zeta$$

$$A(4,19) = A(6,21) = 5\zeta/14^{\frac{1}{2}}$$

$$A(4,32) = A(6,34) = -5 \,.\, 6^{\frac{1}{2}}Dq/7 + 4 \,.\, 6^{\frac{1}{2}}D_S/7 + 5 \,.\, 6^{\frac{1}{2}}D_T/7$$

$$A(5,5) = 18Dq/7 + 12B + 2C - 20D_S/7 - 18D_T/7 + 20\alpha$$

$$A(5,18) = A(5,22) = (3/14)^{\frac{1}{2}}\zeta$$

$$A(5,33) = -100Dq/7 \,.\, 5^{\frac{1}{2}} + 48D_S/980^{\frac{1}{2}} + 200D_T/980^{\frac{1}{2}}$$

$$A(5,45) = 140Dq/350^{\frac{1}{2}} - 140D_T/350^{\frac{1}{2}}$$

$$A(10,10) = A(30,30) = -3Dq + 3\zeta/2 + D_S + 3D_T + 12\alpha$$

$$A(10,22) = A(11,23) = A(12,24) = A(16,28) = A(17,29) = A(18,30) = -15^{\frac{1}{2}}Dq$$

$$A(10,42) = A(11,43) = A(12,44) = A(28,36) = A(29,37) = A(30,38) = -10^{\frac{1}{2}}Dq$$

$$A(11,11) = A(29,29) = -3Dq + D_S + 3D_T + 12\alpha$$

$$A(12,12) = A(28,28) = -3Dq - 3\zeta/2 + D_S = 3D_T + 12\alpha$$

$$A(12,31) = A(28,35) = -(12/7)^{\frac{1}{2}}\zeta$$

$$A(13,13) = A(27,27) = 7Dq + \zeta - 7D_T + 12\alpha$$

$$A(13,25) = A(14,26) = A(15,27) = -5Dq$$

$$A(14,14) = A(26,26) = 7Dq - 7D_T + 12\alpha$$

$$A(14,16) = A(15,17) = A(23,25) = A(24,26) = 5\zeta/20^{\frac{1}{2}}$$

$$A(14,31) = A(26,35) = (4/7)^{\frac{1}{2}}\zeta$$

$$A(15,15) = A(25,25) = 7Dq - \zeta - 7D_T + 12\alpha$$

$$A(15,32) = A(25,34) = -(8/7)^{\frac{1}{2}}\zeta$$

$$A(16,16) = A(24,24) = -Dq + \zeta/2 - 3D_S/5 + 12\alpha$$

$$A(16,31) = A(24,35) = -(4/35)^{\frac{1}{2}}\zeta$$

$$A(16,36) = A(17,37) = A(18,38) = A(22,42) = A(23,43) = A(24,44) = -6^{\frac{1}{2}}Dq + 4 \,.\, 6^{\frac{1}{2}}D_S/5 + 6^{\frac{1}{2}}D_T$$

$$A(17,17) = A(23,23) = -Dq - 3D_S/5 + D_T + 12\alpha$$

$$A(17,19) = A(18,20) = A(20,22) = A(21,23) = (3/2)^{\frac{1}{2}}\zeta$$

$$A(17,32) = A(23,34) = (32/35)^{\frac{1}{2}}\zeta$$

$$A(18,18) = A(22,22) = -Dq - \zeta/2 - 3D_S/5 + D_T + 12\alpha$$

$$A(18,33) = A(22,33) = -(24/35)^{\frac{1}{2}}\zeta$$

$$A(19,19) = A(21,21) = -6Dq - 4D_S/10 + 6D_T + 12\alpha$$

$$A(19,32) = A(21,34) = -(12,35)^{\frac{1}{2}}\zeta$$

$A(19,39) = A(20,40) = A(21,41) = 4Dq + 12D_S/5 - 4D_T$

$A(20,20) = -6Dq - 4D_S/10 + 6D_T + 12\alpha$

$A(20,33) = (36/35)^{\frac{1}{2}}\zeta$

$A(31,31) = A(35,35) = 4Dq/7 + 5B + 2C - 6D_S/7 - 4D_T/7 + 6\alpha$

$A(31,35) = 20Dq/7$

$A(31,36) = A(35,44) = (21/10)^{\frac{1}{2}}\zeta$

$A(32,32) = A(34,34) = -16Dq/7 + 5B + 2C + 6D_S/14 + 32D_T/14 + 6\alpha$

$A(32,37) = A(34,43) = A(32,39) = A(34,41) = (147/140)^{\frac{1}{2}}\zeta$

$A(33,33) = 24Dq/7 + 5B + 2C + 12D_S/14 - 48D_T/14 + 6\alpha$

$A(33,38) = A(33,42) = (49/140)^{\frac{1}{2}}\zeta$

$A(33,40) = (196/140)^{\frac{1}{2}}\zeta$

$A(33,45) = 28D_S/70^{\frac{1}{2}}$

$A(36,36) = A(44,44) = 15B + \zeta/2 - 7D_S/5 + 2\alpha$

$A(37,37) = A(43,43) = 15B - 7D_S/5 + 2\alpha$

$A(37,39) = A(38,40) = A(40,42) = A(41,43) = \zeta/2$

$A(38,38) = A(42,42) = -\zeta/2 + 15B - 7D_S/5 + 2\alpha$

$A(38,45) = A(42,45) = -2^{\frac{1}{2}}\zeta$

$A(39,39) = A(40,40) = A(41,41) = 15B + 14D_S/5 + 2\alpha$

$A(40,45) = 2^{\frac{1}{2}}\zeta$

$A(45,45) = 22B + 7C - 4D_S/5 - 12D_T/5$

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