Analysis of the spectrum of Fe^{2+} in Fe-pyrope garnets

Shen Guo-Yin and Zhao Min-Guang
Institute of Solid State Physics, Sichuan Teachers College, Chengdu 610066, China
(Received 26 January 1984)

The superposition model and the point-charge model have been used to calculate the energy levels of Fe^{2+} at D_2 sites in Fe-pyrope garnet. A number of absorption bands in the near-infrared, visible, and near-ultraviolet region of pyrope are quantitatively assigned to Fe^{2+} at dodecahedral sites. The order of the spin-allowed energy levels is the same as that given by Newman *et al.* [Am. Mineral **63**, 1278 (1978)] and Chuanyi [Bull. Mineral. **104**, 218 (1981)] and the spin-forbidden transitions obtained by using the two models are also in agreement with that determined from absorption spectra (Moore and White [Can. Mineral. **11**, 791 (1972)] and Manning [Can. Mineral. **9**, 237 (1967)]). In our calculation only two parameters are needed for the superposition model and one parameter for the point-charge model since the self-consistent-field (SCF) d orbital for Fe^{2+} proposed by Zhao and Du [Phys. Rev B **28**, 6481 (1983)] has been used. The results agree with both optical-absorption and Mössbauer spectral data and also show that the Fe^{2+} at dodecahedral sites is of a highly ionic nature.

I. INTRODUCTION

The study of the d-d spectra of garnets is of interest because the crystals can contain transition metals, and also because these cations can be distributed between dodecahedral, octahedral, and tetrahedral sites. Among them the main cation is Fe^{2+}, which is predominantly located at dodecahedral sites with D_2 point symmetry. The electronic spectra of Fe^{2+} in iron-bearing garnets have been studied by many workers (Moore and White,[1] Burns,[2] Manning,[3] Slack and Chrenko,[4] Lin,[5] and Newman *et al.*[6]). It is generally agreed that Fe^{2+} is responsible for a group of three strong near-infrared bands due to spin-allowed transitions and for a number of weak, sharp bands in the visible region due to spin-forbidden transitions.

Recently, Newman *et al.*[6] and Lin[5] gave the same order of the spin-allowed energy levels of Fe^{2+} obtained by using the superposition model and the point-charge model (we use this form to represent the point-charge ionic bonding model throughout the paper), respectively. Moore and White[1] reached definite assignments for the complicated visible bands of the pyralspites *qualitatively*, and pointed out that a large portion of the spectrum is dominated by the spin-forbidden bands of Fe^{2+}, split by the highly distorted orthorhombic field of the eightfold sites. Yet we know of no theoretical report using the actual symmetry D_2 for the spin-forbidden transitions of Fe^{2+}. This paper will report the results obtained by using both the superposition and the point-charge models, which are in agreement with both optical-absorption and Mössbauer spectral data. In calculating the energy levels, we have employed only two parameters for the superposition model and one parameter for the point-charge model, having adopted Zhao and Du's[7] self-consistent-field (SCF) d orbital for Fe^{2+}.

II. THEORETICAL ANALYSIS

Huggins[8] remarked that the predominant contributions to the crystal field in this system appear to arise from ions in the first coordination sphere. The symmetry of the Fe^{2+}-O_8 dodecahedron is D_2, and the Fe^{2+} ions occupy the $24c$ position of space group $Ia\,3d$ (Novak and Gibbs[9]). There are five quintet states and a number of triplet states for Fe^{2+}, with $3d^6$ configuration, on the D_2 sites. In the present work we carry out calculations using two models, i.e., the superposition model and the point-charge model. In fact, the point-charge model may be regarded as a special case of the superposition model where the power-law exponents are $t=3$, $t=5$.

A. Point-charge model

The one-electron crystal-field potential with garnet D_2 symmetry can be written as

$$V_i=\sum_{k=2,4}\sum_{a,b} r^k v_{ka}^{(b)} Z_{ka}^{(b)}(\theta_i,\phi_i)$$

$$=\tfrac{4}{5}\sqrt{5\pi}eq\,\beta\frac{1}{R_A^3}r_i^2 Z_{20}(\theta_i,\phi_i)+\tfrac{4}{5}\sqrt{15\pi}eq\,\epsilon\frac{1}{R_A^3}r_i^2 Z_{22}^c(\theta_i,\phi_i)+\tfrac{1}{3}\sqrt{\pi}eq\,\alpha\frac{1}{R_A^5}r_i^4 Z_{40}(\theta_i,\phi_i)$$

$$+\tfrac{2}{3}\sqrt{5\pi}eq\,\delta\frac{1}{R_A^5}r_i^4 Z_{42}^c(\theta_i,\phi_i)+\tfrac{1}{3}\sqrt{35\pi}eq\,\nu\frac{1}{R_A^5}r_i^4 Z_{44}^c(\theta_i,\phi_i)\,, \tag{1}$$

 ©1984 The American Physical Society

where the geometric parameters $\alpha,\beta,\nu,\delta,\epsilon$ are of the same form as that used by Runciman and Sengupta;[10] $Z_{ka}^{(b)}(\theta_i,\phi_i)$ denotes real spherical harmonic functions; r_i,θ_i,ϕ_i are the coordinates of the d electrons in Fe^{2+}; e denotes the proton charge; q is the equivalent charge of the ligand O^{2-}.

Fe^{2+} is thus subject to the crystal-field potential

$$V=\sum_{i=1}^{6} V_i \ . \tag{2}$$

Using the proper basis function of D_2 symmetry, we obtain, in the weak-field scheme, the Hamiltonian matrix elements of the triplet states $^3A_1$ (9×9 matrix), $^3B_1$ (12×12 matrix), $^3B_2$ (12×12 matrix), $^3B_3$ (12×12 matrix), and of the quintet states $^5B_1$, $^5B_2$, $^5B_3$, and $^5A_1$ (2×2 matrix). The matrix elements (see Appendix) are expressions of the Racah parameters B,C, the Trees correction α, and the crystal-field parameters which are of the form

$$\begin{aligned} &D_s=\tfrac{2}{7}eq\,\beta\frac{1}{R_A^3}\langle r^2\rangle,\quad D_q=-\tfrac{1}{42}eq\,\alpha\frac{1}{R_A^5}\langle r^4\rangle\ ,\\ &D_\tau=-\tfrac{5}{6}eq\,\nu\frac{1}{R_A^5}\langle r^4\rangle,\quad D_\xi=-\tfrac{2}{7}eq\,\epsilon\frac{1}{R_A^3}\langle r^2\rangle\ ,\\ &D_\eta=\tfrac{5}{42}eq\,\delta\frac{1}{R_A^5}\langle r^4\rangle\ . \end{aligned} \tag{3}$$

In our calculation, Zhao and Du's[7] d orbital for Fe^{2+} has been used, which gives

$$\begin{aligned} R_\alpha(r)=0.5692&\left[\frac{11.0182^7}{6!}\right]^{1/2}r^2\exp(-5.51903r)\\ &+0.6500\left[\frac{3.54794^7}{6!}\right]^{1/2}r^2\exp(-1.77397r)\ . \end{aligned} \tag{4}$$

The expectation values of r^2 and r^4 are

$$\langle r^2\rangle=2.2949\ \text{a.u.},\quad \langle r^4\rangle=14\ \text{a.u.}\ ,$$

and the Racah parameters

$$B=947\ \text{cm}^{-1},\quad C=3375\ \text{cm}^{-1}\ . \tag{5}$$

Thus the crystal-field parameters D_s, D_q, D_t, D_ξ, D_η can be obtained as long as we know the values of the geometric parameters $\alpha,\beta,\nu,\delta,\epsilon$ that can be determined by crystallographic data (Novak and Gibbs[9]). Finally, after solving several determinants, we obtain both the spin-allowed and the spin-forbidden transitions of Fe^{2+} in garnet D_2 sites. The results are given in Table I.

B. Superposition model

Newman *et al.*[6] gave the superposition-model equation for the crystal-field parameters at garnet D_2 sites in the form

$$A_n^m\langle r^n\rangle=\bar{A}_n(R)\left[K_m^n(A)+\left[\frac{R_A}{R_B}\right]^{t_n}K_m^n(B)\right]\ , \tag{6}$$

where $K_m^n(A)$, $K_m^n(B)$ can be calculated from the angular coordination (Newman and Urban[11]); the $\bar{A}_n(R)$ are intrinsic parameters; the t_n are power-law exponents. In the present paper we employ the SCF d orbital for Fe^{2+} given in (4), so the intrinsic parameters $\bar{A}_n(R)$ can be calculated as

$$\begin{aligned} &\bar{A}_4=\tfrac{1}{8}\frac{eq\langle r^4\rangle}{R_A^5}=618\ \text{cm}^{-1}\ ,\\ &\bar{A}_2=\tfrac{1}{2}\frac{eq\langle r^2\rangle}{R_A^3}=7007\ \text{cm}^{-1}\ , \end{aligned} \tag{7}$$

which is in good accord with the values obtained by Newman *et al.*:[6] $\bar{A}_4=596\ \text{cm}^{-1}$, $\bar{A}_2=7060\ \text{cm}^{-1}$. It seems to be true that Zhao and co-workers' d-orbital theory is suitable for both the point-charge model and the superposition model.

With the assumption of the power-law exponents $t_2=3$, $t_4=7$, the geometric parameters α,β,ν,δ and ϵ are now of the form

$$\begin{aligned} &\alpha=8\left[K_4^0(A)+\left[\frac{R_A}{R_B}\right]^7K_4^0(B)\right]\ ,\\ &\beta=2\left[K_2^0(A)+\left[\frac{R_A}{R_B}\right]^3K_2^0(B)\right]\ ,\\ &\nu=\tfrac{8}{35}\left[K_4^4(A)+\left[\frac{R_A}{R_B}\right]^7K_4^4(B)\right]\ ,\\ &\delta=\tfrac{2}{5}\left[K_4^2(A)+\left[\frac{R_A}{R_B}\right]^7K_4^2(B)\right]\ ,\\ &\epsilon=\tfrac{2}{3}\left[K_2^2(A)+\left[\frac{R_A}{R_B}\right]^3K_2^2(B)\right]\ . \end{aligned} \tag{8}$$

Again, from (3), (5), and (8) we have the Racah parameters B,C and crystal-field parameters D_s,D_q,D_t,D_ξ,D_η. Therefore, both the spin-allowed and the spin-forbidden energy levels of Fe^{2+} in garnet D_2 sites can be obtained. All of the results are shown in Table I.

III. DISCUSSION

A. Comparison of models

As shown in Table I, the results obtained by using two models are nearly the same, which indicates that there are some common points between those two models. Although the superposition model, unlike the point-charge model, makes no assumptions about the mechanics (or magnitude) of ligand contributions which contain covalency and overlap as well as electrostatic interactions, etc. (Newman[15] and Newman and Chen[16]), the power-law exponents we have chosen, $t_2=3$, $t_4=7$, are close to a special case $t_2=3$, $t_4=5$, i.e., the point-charge model. The conditions in our calculation, $t_2=3$, $t_4=7$ for the superposition model and $q=1.88e$ for the point-charge model, show that Fe^{2+} at dodecahedral D_2 sites in pyrope garnet is of a highly ionic nature. It is very interesting that the Mössbauer data (Amthauer *et al.*[17]), the isomer

TABLE I. Observed and calculated transition frequencies of both spin-allowed and spin-forbidden Fe^{2+} in Fe-pyrope garnet. All quantities are given in cm^{-1}.

Transition[a]	Observed data[b]	Calculated values[c] Superposition model[d]	Calculated values[c] Point-charge model[e]
$^5A_1(D)\rightarrow{}^5B_1(D)$	1100[f]	1547	1544
$^5B_3(D)$	4500	4485	4729
$^5A_1(D)$	6100	6173	6153
$^5B_2(D)$	7800	8135	7831
$^3B_3(H)$	14 500	15 001	15 317
$^3B_1(H)$	16 300	16 598	16 649
$^3B_2(H)$	17 400	17 573	17 341
$^3B_2(H),{}^3B_1(H)$	19 100	18 759, 19 485	
$^3B_2(H)^*$			18 988
$^3A_1(H)$	19 800	20 061	
$^3B_1(H)^*$			19 841
$^3A_1(F)$	20 100	20 501	
$^3A_1(H)^*,{}^3A_1(F)^*$			20 149, 20 582
$^3B_3(H),{}^3B_2(F)$	20 900	21 025, 21 086	
$^3B_3(H)^*$			20 864
$^3B_1(P)$	21 600	21 610	
$^3B_2(F)^*,{}^3B_1(P)^*$			21 323, 21 538
$^3B_1(F),{}^3B_3(F)$	22 800	22 620, 22 796	22 545, 22 627
Fe^{3+}	23 400		
$^3A_1(G)$	23 700	24 090	24 011
$^3B_3(F),{}^3B_1(H)$	24 300 24 500	24 463, 24 465	24 509, 24 684
$^3A_1(G),{}^3B_3(H)$	25 000	24 924, 25 169	24 991, 25 365
	27 200	26 469	26 520
		26 739	26 617
		26 909	26 728
		26 912	26 822
		27 084	26 935
		27 167	27 327
	29 000[g]	28 566	28 330
		28 934	29 034
		⋮	⋮

[a]The states with an asterisk are from the point-charge model if they are different from that which are from the superposition model.

[b]The data are almost the same among different workers. Here the values are from Moore and White (Refs. 1 and 12).

[c]The Racah-Trees correction α is, as usual, equal to 85 cm^{-1} [Zhao and Du (Ref. 7)]. The Racah parameters $B=947$ cm^{-1}, $C=3375$ cm^{-1} determined by using the d-orbital theory [Zhao and co-workers (Refs. 7, 13, and 14)].

[d]With the assumption of the power-law exponents $t_2=3$, $t_4=7$, the crystal-field parameters $D_s=-126$ cm^{-1}, $D_q=592$ cm^{-1}, $D_t=-2181$ cm^{-1}, $D_\xi=-467$ cm^{-1}, $D_\eta=106$ cm^{-1}.

[e]Using the equivalent charge of the ligand O^{2-}, $q=1.88e$, we have $D_s=-118$ cm^{-1}, $D_q=587$ cm^{-1}, $D_t=-2158$ cm^{-1}, $D_\xi=-439$ cm^{-1}, $D_\eta=58$ cm^{-1}.

[f]Data determined from Mössbauer analysis [Huggins (Ref. 8)].

[g]Data from Manning (Ref. 3).

shift, and quadrupole splitting of Fe^{2+} at the garnet D_2 sites are also indicative of a highly ionic state. This shows that the fitting parameters we chose are reasonable for calculating the energy levels of Fe^{2+} in garnet D_2 sites.

B. Spin-allowed transitions

There are five quintet states, i.e., $^5B_1$, $^5B_2$, $^5B_3$, and two $^5A_1$ states for Fe^{2+} at a D_2 site. Therefore, four spin-allowed transitions are expected. The three intense near-infrared bands at 4500, 6100, and 7800 cm^{-1} are assigned to transitions from the $^5A_1$ ground state to the $^5B_3$, $^5A_1$, $^5B_2$ states, respectively. Our theoretical value about the transition $^5A_1\rightarrow{}^5B_1$ is also in agreement with the Mössbauer data at 1100 cm^{-1} (Huggins,[8] Amthauer *et al.*[17]). The order of the energy levels obtained in this work is the same as that obtained by Lin[5] and Newman *et al.*[6]

TABLE II. The assignments of spin-forbidden bands of Fe-pyrope garnet. All quantities are given in cm^{-1}.

Observed	Moore and White (Ref. 1)	Present work[a]	
14 500	$^3B_1(H),^3B_2(H),^3B_3(H)$	$^3B_3(H)$	15 001
16 300		$^3B_1(H)$	16 598
17 400		$^3B_2(H)$	17 573
19 100	$^3B_1(H),^3A_1(H)$	$^3B_2(H),^3B_1(H)$	18 759,19 485
19 800		$^3A_1(H)$	20 061
20 100		$^3A_1(F)$	20 501

[a]Results of the superposition model.

C. Spin-forbidden transitions

As of yet, there is no theoretical work concerning the spin-forbidden transitions of Fe^{2+} in garnet D_2 sites, but there exist a lot of reports about the spectra of garnets (Moore and White,[1] Burns,[2] Manning,[3] etc.). Our calculated results and assignments are given in Table I and a few remarks about the spectrum are needed.

(i) The bands near 14 500, 16 300, and 17 400 cm^{-1} have been assigned to the transitions to $^3B_3(H)$, $^3B_1(H)$, and $^3B_2(H)$ states, respectively. The frequencies of those three bands are in close agreement with the calculations performed in this work. D_2 group designations $^3B_1(H)$, $^3B_2(H)$, and $^3B_3(H)$ are from the D_2 splitting of the O_h group designation $^3T_1(H)$. It shows that the distortion of the crystal field may be an important reason for the complexity of the spectra.

(ii) Moore and White[1] pointed out that three bands near 23 700, 24 300, and 24 500 cm^{-1} are due to Mn^{2+} according to Beer's law dependence. Since these three bands are very weak, the intensity of these cannot be measured accurately. Furthermore, our calculated results are in good agreement with the frequencies observed. These three bands might arise from Fe^{2+} at the D_2 sites. More experimental work may be useful in this respect.

(iii) It can be seen from Moore and White (Ref. 1, Fig. 5) and Manning (Ref. 3, Fig. 2) that the band near 27 200 cm^{-1} is stronger and wider than its neighbor. We assigned this band to the transitions to several states as given in Table I. More precise experiments are needed in this respect.

(iv) Table II shows our quantitative assignments for the bands in the lower-frequency portion of the visible spectrum and the assignments reached qualitatively by Moore and White.[1] They are very similar to each other.

IV. CONCLUSION

A calculation based on the superposition model and the point-charge model using the d orbital for Fe^{2+} proposed by Zhao *et al.* gives spin-allowed energy levels for Fe^{2+} at garnet D_2 sites of the same magnitude as that given by Lin[5] and Newman *et al.*[6] and also gives the spin-forbidden transitions which are in close agreement with optical absorption and Mössbauer spectral data. Two parameters, $t_2=3$, $t_4=7$, for the superposition model and one parameter, $q=1.88e$, for the point-charge model allow us to derive satisfactory results that are nearly the same as each other. The assumed parameters indicate that Fe^{2+} at dodecahedral D_2 sites in pyrope garnet is of a highly ionic nature, which is in accord with isomer shift and quadrupole splitting data (Amthauer *et al.*[17]). The definite assignments in Table I show that the distortion of the crystal field plays an important role in the complexity of the spectra of Fe-pyrope garnets, since our results are obtained using the actual symmetry D_2 of the ions surrounding the Fe^{2+}.

ACKNOWLEDGMENT

We thank Professor D. J. Newman for helpful discussions.

APPENDIX: ENERGY MATRICES OF A $d^4(d^6)$ CONFIGURATION IN A DODECAHEDRAL D_2 SYMMETRY FIELD

So far, no triplet energy matrices of $d^4(d^6)$ configuration in a D_2 symmetry field have been reported. Here we

TABLE III. The basis functions of irreducible representations of D_2 point-group symmetry.

SO_3	O_h	D_{4h}	D_2	Functions
S	A_1	A_1	A_1	$\|0,0\rangle$
	T_1	A_2	B_1	$-i\|1,1\rangle$
P		E	B_2	$-\frac{1}{\sqrt{2}}(\|1,1\rangle+\|1,-1\rangle)$
			B_3	$\frac{i}{\sqrt{2}}(\|1,1\rangle-\|1,-1\rangle)$
	E	A_1	A_1	$\|2,0\rangle$

TABLE III. (*Continued*).

SO_3	O_h	D_{4h}	D_2	Functions
		B_1	A_1	$\frac{1}{\sqrt{2}}(\|2,2\rangle+\|2,-2\rangle)$
D	T_2	B_2	B_1	$\frac{i}{\sqrt{2}}(\|2,2\rangle-\|2,-2\rangle)$
		E	B_2	$\frac{1}{\sqrt{2}}(\|2,1\rangle-\|2,-1\rangle)$
			B_3	$\frac{i}{\sqrt{2}}(\|2,1\rangle+\|2,-1\rangle)$
	T_1	A_2	B_1	$-i\|3,0\rangle$
		E	B_2	$-\frac{1}{4}[\sqrt{5}(\|3,3\rangle+\|3,-3\rangle)-\sqrt{3}(\|3,1\rangle+\|3,-1\rangle)]$
			B_3	$-\frac{i}{4}[\sqrt{5}(\|3,3\rangle-\|3,-3\rangle)+\sqrt{3}(\|3,1\rangle-\|3,-1\rangle)]$
F	A_2	B_1	A_1	$\frac{1}{\sqrt{2}}(\|3,2\rangle-\|3,-2\rangle)$
	T_2	B_2	B_1	$\frac{i}{\sqrt{2}}(\|3,2\rangle+\|3,-2\rangle)$
		E	B_2	$\frac{1}{4}[\sqrt{3}(\|3,3\rangle+\|3,-3\rangle)+\sqrt{5}(\|3,1\rangle+\|3,-1\rangle)]$
			B_3	$\frac{i}{4}[\sqrt{3}(\|3,3\rangle-\|3,-3\rangle)-\sqrt{5}(\|3,1\rangle-\|3,-1\rangle)]$
	A_1	A_1	A_1	$\frac{1}{\sqrt{24}}[\sqrt{14}\|4,0\rangle-\sqrt{5}(\|4,4\rangle+\|4,-4\rangle)]$
	T_1	A_2	B_1	$\frac{i}{\sqrt{2}}(\|4,4\rangle-\|4,-4\rangle)$
		E	B_2	$\frac{1}{4}[(\|4,3\rangle-\|4,-3\rangle)+\sqrt{7}(\|4,1\rangle-\|4,-1\rangle)]$
			B_3	$\frac{i}{4}[(\|4,3\rangle+\|4,-3\rangle)-\sqrt{7}(\|4,1\rangle+\|4,-1\rangle)]$
G	T_2	B_2	B_1	$\frac{i}{\sqrt{2}}(\|4,2\rangle-\|4,-2\rangle)$
		E	B_2	$-\frac{1}{4}[\sqrt{7}(\|4,3\rangle-\|4,-3\rangle)-(\|4,1\rangle-\|4,-1\rangle)]$
			B_3	$-\frac{i}{4}[\sqrt{7}(\|4,3\rangle+\|4,-3\rangle)+\|4,-3\rangle)+(\|4,1\rangle+\|4,-1\rangle)]$
	E	A_1	A_1	$-\frac{1}{\sqrt{24}}[\sqrt{10}\|4,0\rangle+\sqrt{7}(\|4,4\rangle+\|4,-4\rangle)]$
		B_1	A_1	$\frac{1}{\sqrt{2}}(\|4,2\rangle+\|4,-2\rangle$
	E	A_1	A_1	$-\frac{1}{\sqrt{2}}(\|5,2\rangle-\|5,-2\rangle)$
		B_1	A_1	$-\frac{1}{\sqrt{2}}(\|5,4\rangle-\|5,-4\rangle)$
		A_2	B_1	$-\frac{i}{\sqrt{2}}(\|5,2\rangle+\|5,-2\rangle)$
	T_1	A_2	B_1	$-\frac{i}{\sqrt{2}}(\|5,2\rangle+\|5,-2\rangle)$
		E	B_2	$\frac{1}{8}[\sqrt{14}(\|5,1\rangle+\|5,-1\rangle)-\sqrt{3}(\|5,3\rangle+\|5,-3\rangle+\sqrt{15}(\|5,5\rangle+\|5,-5\rangle)]$
			B_3	$-\frac{i}{8}[\sqrt{14}(\|5,1\rangle-\|5,-1\rangle)+\sqrt{3}(\|5,3\rangle-\|5,-3\rangle)+\sqrt{15}(\|5,5\rangle-\|5,-5\rangle)]$
H	T_1	A_2	B_1	$i\|5,0\rangle$
		E	B_2	$\frac{1}{16}[\sqrt{30}(\|5,1\rangle+\|5,-1\rangle)-\sqrt{35}(\|5,3\rangle+\|5,-3\rangle)-3\sqrt{7}(\|5,5\rangle+\|5,-5\rangle)$
			B_3	$-\frac{i}{16}[\sqrt{30}(\|5,1\rangle-\|5,-1\rangle)+\sqrt{35}(\|5,3\rangle-\|5,-3\rangle)-3\sqrt{7}(\|5,5\rangle-\|5,-5\rangle)]$
	T_2	B_2	B_1	$-\frac{i}{\sqrt{2}}(\|5,4\rangle-\|5,-4\rangle)$
		E	B_2	$\frac{1}{16}\left[\frac{1}{\sqrt{42}}(\|5,1\rangle+\|5,-1\rangle)+9(\|5,3\rangle+\|5,-3\rangle)-\sqrt{5}(\|5,5\rangle+\|5,-5\rangle)\right]$
			B_3	$-\frac{i}{16}\left[\frac{1}{\sqrt{42}}(\|5,1\rangle-\|5,-1\rangle)-9(\|5,3\rangle-\|5,-3\rangle)-\sqrt{5}(\|5,5\rangle-\|5,-5\rangle)\right]$

TABLE IV. The triplet $^3A_1$ energy matrix elements,

$\langle {}^3A_1({}^3D)|\sum\hat{V}|{}^3A_1({}^3D)\rangle \equiv a^1_{1,1}$, $\langle {}^3A_1({}^5D)|\sum\hat{V}|{}^3A_1({}^5D')\rangle \equiv a^1_{1,2}$
$= a^1_{2,1} \equiv \langle {}^3A_1({}^5D')|\sum\hat{V}|{}^3A_1({}^5D)\rangle$, $\langle {}^3A_1({}^3D)|\sum\hat{V}|{}^3A_1({}^3F_1)\rangle \equiv a^1_{1,3}$
$= a^1_{3,1} \equiv \langle {}^3A_1({}^3F_1)|\sum\hat{V}|{}^3A_1({}^3D)\rangle, \ldots, \langle {}^3A_1({}^3H')|\sum\hat{V}|{}^3A_1({}^3H')\rangle \equiv a^1_{9,9}$.

$^3A_1$	^3D	$^3D'$	$^3F_1$	$^3F_2$	^3G	$^3G'$	$^3G''$	^3H	$^3H'$
^3D	$a^1_{1,1}$	$a^1_{1,2}$	$a^1_{1,3}$	$a^1_{1,4}$	$a^1_{1,5}$	$a^1_{1,6}$	$a^1_{1,7}$	$a^1_{1,8}$	$a^1_{1,9}$
$^3D'$		$a^1_{2,2}$	$a^1_{2,3}$	$a^1_{2,4}$	$a^1_{2,5}$	$a^1_{2,6}$	$a^1_{2,7}$	$a^1_{2,8}$	$a^1_{2,9}$
$^3F_1$			$a^1_{3,3}$	$a^1_{3,4}$	$a^1_{3,5}$	$a^1_{3,6}$	$a^1_{3,7}$	$a^1_{3,8}$	$a^1_{3,9}$
$^3F_2$				$a^1_{4,4}$	$a^1_{4,5}$	$a^1_{4,6}$	$a^1_{4,7}$	$a^1_{4,8}$	$a^1_{4,9}$
^3G					$a^1_{5,5}$	$a^1_{5,6}$	$a^1_{5,7}$	$a^1_{5,8}$	$a^1_{5,9}$
$^3G'$						$a^1_{6,6}$	$a^1_{6,7}$	$a^1_{6,8}$	$a^1_{6,9}$
$^3G''$							$a^1_{7,7}$	$a^1_{7,8}$	$a^1_{7,9}$
^3H								$a^1_{8,8}$	$a^1_{8,9}$
$^3H'$									$a^1_{9,9}$

where $a^1_{i,j}$ $(=a^1_{j,i})$ are as follows:

$$a^1_{1,1}=\tfrac{1}{21}(6D_s-11D_q-11D_t)-5B+4C+6\alpha,\quad a^1_{1,2}=\frac{2\sqrt{3}}{21}(-3D_\xi+11D_\eta)$$
$$a^1_{1,3}=\frac{4\sqrt{7}}{21}(3D_s+5D_q-D_t),\quad a^1_{1,4}=\frac{\sqrt{7}}{7}(-4D_s+5D_q-D_t)$$
$$a^1_{1,5}=\frac{\sqrt{5}}{35}(20D_s+45D_q+3D_t),\quad a^1_{1,6}=\frac{2\sqrt{15}}{105}(40D_\xi+33D_\eta)$$
$$a^1_{1,7}=\frac{2\sqrt{21}}{21}(4D_\xi-3D_\eta),\quad a^1_{1,8}=\frac{\sqrt{70}}{105}(-35D_q+D_t)$$
$$a^1_{1,9}=\frac{2\sqrt{210}}{15}D_\eta$$

$$a^1_{2,2}=\tfrac{1}{7}(-2D_s-22D_q)-5B+4C+6\alpha,\quad a^1_{2,3}=\frac{4\sqrt{21}}{21}(3D_\xi-4D_\eta)$$
$$a^1_{2,4}=\frac{4\sqrt{21}}{7}(-D_\xi-D_\eta),\quad a^1_{2,5}=\frac{4\sqrt{15}}{35}(-5D_\xi+2D_\eta),\quad a^1_{2,6}=\frac{\sqrt{5}}{35}(-20D_s+25D_q-7D_t)$$
$$a^1_{2,7}=\frac{\sqrt{7}}{7}(4D_s-5D_q-D_t),\quad a^1_{2,8}=-\frac{2\sqrt{210}}{15}D_\eta,\quad a^1_{2,9}=\frac{2\sqrt{70}}{35}D_t$$

$$a^1_{3,3}=\tfrac{1}{3}(7D_q+D_t)-2B+7C+12\alpha,\quad a^1_{3,4}=12B,\quad a^1_{3,5}=\frac{4\sqrt{35}}{35}(3D_s+5D_q-D_t)$$
$$a^1_{3,6}=\frac{2\sqrt{105}}{105}(-3D_\xi+4D_\eta),\quad a^1_{3,7}=\frac{2\sqrt{3}}{3}(-3D_\xi+4D_\eta),\quad a^1_{3,8}=\frac{2\sqrt{10}}{15}(-3D_s-5D_q+D_t)$$
$$a^1_{3,9}=\frac{2\sqrt{30}}{15}(3D_\xi-4D_\eta)$$

$$a^1_{4,4}=\tfrac{1}{2}(-7D_q-D_t)-8B+4C+12\alpha,\quad a^1_{4,5}=\frac{\sqrt{35}}{70}(4D_s-5D_q+D_t)$$
$$a^1_{4,6}=\frac{\sqrt{105}}{105}(-D_\xi-D_\eta),\quad a^1_{4,7}=\frac{\sqrt{3}}{3}(-D_\xi-D_\eta),\quad a^1_{4,8}=\frac{\sqrt{10}}{10}(-4D_s+5D_q-D_t),\quad a^1_{4,9}=\frac{2\sqrt{30}}{5}(D_\xi+D_\eta)$$

$$a^1_{5,5}=\tfrac{1}{70}(8D_s+165D_q-45D_t)-12B+4C+20\alpha,\quad a^1_{5,6}=\frac{\sqrt{3}}{35}(-11D_\xi-25D_\eta)$$

TABLE IV. (*Continued*).

$^3A_1$	^3D	$^3D'$	$^3F_1$	$^3F_2$	^3G	$^3G'$	$^3G''$	^3H	$^3H'$

$a^1_{5,7}=\frac{\sqrt{105}}{35}(D_\xi-13D_\eta)$, $a^1_{5,8}=\frac{\sqrt{14}}{70}(-28D_s-35D_q-5D_t)$, $a^1_{5,9}=-\frac{2\sqrt{42}}{5}D_\xi$

$a^1_{6,6}=\frac{1}{70}(-8D_s-235D_q-35D_t)-12B+4C+20\alpha$, $a^1_{6,7}=\frac{\sqrt{35}}{70}(-4D_s+5D_q+D_t)$

$a^1_{6,8}=\frac{\sqrt{42}}{15}(4D_\xi+5D_\eta)$, $a^1_{6,9}=\frac{\sqrt{14}}{70}(28D_s-35D_q+5D_t)$

$a^1_{7,7}=\frac{1}{2}(-7D_q+D_t)-12B+4C+20\alpha$, $a^1_{7,8}=\frac{\sqrt{30}}{15}(-8D_\xi-D_\eta)$, $a^1_{7,9}=\frac{\sqrt{10}}{10}(4D_s-5D_q-D_t)$

$a^1_{8,8}=\frac{1}{15}(-6D_s-10D_q-10D_t)-17B+4C+30\alpha$, $a^1_{8,9}=\frac{2\sqrt{3}}{15}(-3D_\xi-10D_\eta)$

$a^1_{9,9}=\frac{2}{5}(D_s-10D_q)-17B+4C+30\alpha$

TABLE V. The triplet ^3B_k ($k=1$, 2, or 3) energy matrix elements,

$\langle {}^3B_k({}^3P_1)|\sum\hat{V}|{}^3B_k({}^3P_1)\rangle\equiv b^k_{1,1}$, $\langle {}^3B_k({}^3P_1)|\sum\hat{V}|{}^3B_k({}^3P_2)\rangle\equiv b^k_{1,2}$

$=b^k_{2,1}\equiv\langle {}^3B_k({}^3P_2)|\sum\hat{V}|{}^3B_k({}^3P_1)\rangle,\ldots,\langle {}^3B_k({}^3H'')|\sum\hat{V}|{}^3B_k({}^3H'')\rangle\equiv b^k_{12,12}$.

^3B_k	$^3P_1$	$^3P_2$	^3D	$^3F_1$	$^3F_1'$	$^3F_2$	$^3F_2'$	^3G	$^3G'$	^3H	$^3H'$	$^3H''$
$^3P_1$	$b^k_{1,1}$	$b^k_{1,2}$	$b^k_{1,3}$	$b^k_{1,4}$	$b^k_{1,5}$	$b^k_{1,6}$	$b^k_{1,7}$	$b^k_{1,8}$	$b^k_{1,9}$	$b^k_{1,10}$	$b^k_{1,11}$	$b^k_{1,12}$
$^3P_2$		$b^k_{2,2}$	$b^k_{2,3}$	$b^k_{2,4}$	$b^k_{2,5}$	$b^k_{2,6}$	$b^k_{2,7}$	$b^k_{2,8}$	$b^k_{2,9}$	$b^k_{2,10}$	$b^k_{2,11}$	$b^k_{2,12}$
^3D			$b^k_{3,3}$	$b^k_{3,4}$	$b^k_{3,5}$	$b^k_{3,6}$	$b^k_{3,7}$	$b^k_{3,8}$	$b^k_{3,9}$	$b^k_{3,10}$	$b^k_{3,11}$	$b^k_{3,12}$
$^3F_1$				$b^k_{4,4}$	$b^k_{4,5}$	$b^k_{4,6}$	$b^k_{4,7}$	$b^k_{4,8}$	$b^k_{4,9}$	$b^k_{4,10}$	$b^k_{4,11}$	$b^k_{4,12}$
$^3F_1'$					$b^k_{5,5}$	$b^k_{5,6}$	$b^k_{5,7}$	$b^k_{5,8}$	$b^k_{5,9}$	$b^k_{5,10}$	$b^k_{5,11}$	$b^k_{5,12}$
$^3F_2$						$b^k_{6,6}$	$b^k_{6,7}$	$b^k_{6,8}$	$b^k_{6,9}$	$b^k_{6,10}$	$b^k_{6,11}$	$b^k_{6,12}$
$^3F_2'$							$b^k_{7,7}$	$b^k_{7,8}$	$b^k_{7,9}$	$b^k_{7,10}$	$b^k_{7,11}$	$b^k_{7,12}$
^3G								$b^k_{8,8}$	$b^k_{8,9}$	$b^k_{8,10}$	$b^k_{8,11}$	$b^k_{8,12}$
$^3G'$									$b^k_{9,9}$	$b^k_{9,10}$	$b^k_{9,11}$	$b^k_{9,12}$
^3H										$b^k_{10,10}$	$b^k_{10,11}$	$b^k_{10,12}$
$^3H'$											$b^k_{11,11}$	$b^k_{11,12}$
$^3H''$												$b^k_{12,12}$

where $b^1_{i,j}$ ($=b^1_{j,i}$) are as follows:

$b^1_{1,1}=\frac{14}{15}D_s-7B+7C+2\alpha$, $b^1_{1,2}=-\frac{4\sqrt{14}}{15}D_s+4\sqrt{14}B$, $b^1_{1,3}=-\frac{8\sqrt{105}}{15}D_\xi$, $b^1_{1,4}=\frac{4}{15}(3D_s+5D_q)$

$b^1_{1,5}=\frac{4\sqrt{15}}{15}(D_\xi+D_\eta)$, $b^1_{1,6}=\frac{4}{15}(6D_s-25D_q)$, $b^1_{1,7}=\frac{4\sqrt{15}}{15}(2D_\xi-5D_\eta)$

$b^1_{1,8}=\frac{4\sqrt{3}}{15}D_t$, $b^1_{1,9}=-\frac{4\sqrt{21}}{15}D_\eta$, $b^1_{1,10}=-\frac{2\sqrt{2}}{5}D_t$, $b^1_{1,11}=\frac{28\sqrt{6}}{15}D_\eta$, $b^1_{1,12}=\frac{2\sqrt{70}}{3}D_q$

$b^1_{2,2}=-\frac{38}{15}D_s-3B+4C+2\alpha$, $b^1_{2,3}=-\frac{8\sqrt{30}}{15}D_\xi$, $b^1_{2,4}=\frac{2\sqrt{14}}{105}(33D_s-50D_q)$

TABLE V. (*Continued*).

^3B_k	$^3P_1$	$^3P_2$	^3D	$^3F_1$	$^3F_1'$	$^3F_2$	$^3F_2'$	^3G	$^3G'$	^3H	$^3H'$	$^3H''$

$b^1_{2,5}=\frac{2\sqrt{210}}{105}(11D_\xi-10D_\eta)$, $b^1_{2,6}=\frac{\sqrt{14}}{105}(24D_s+5D_q)$, $b^1_{2,7}=\frac{\sqrt{210}}{105}(8D_\xi+D_\eta)$

$b^1_{2,8}=-\frac{17\sqrt{42}}{105}D_t$, $b^1_{2,9}=\frac{17\sqrt{6}}{15}D_\eta$, $b^1_{2,10}=\frac{2\sqrt{7}}{35}D_t$, $b^1_{2,11}=-\frac{4\sqrt{21}}{15}D_\eta$, $b^1_{2,12}=-\frac{2\sqrt{5}}{3}D_q$

$b^1_{3,3}=\frac{1}{21}(6D_s-11D_q+11D_t)-5B+4C+6\alpha$, $b^1_{3,4}=\frac{4\sqrt{105}}{105}(3D_\xi+10D_\eta)$

$b^1_{3,5}=\frac{4\sqrt{7}}{21}(3D_s+5D_q+D_t)$, $b^1_{3,6}=\frac{2\sqrt{105}}{35}(-2D_\xi+5D_\eta)$, $b^1_{3,7}=\frac{\sqrt{7}}{7}(-4D_s+5D_q+D_t)$

$b^1_{3,8}=\frac{2\sqrt{35}}{105}(-10D_\xi-3D_\eta)$, $b^1_{3,9}=\frac{\sqrt{5}}{35}(20D_s+45D_q-3D_t)$, $b^1_{3,10}=\frac{2\sqrt{210}}{15}D_\eta$

$b^1_{3,11}=-\frac{\sqrt{70}}{105}(35D_q+D_t)$, $b^1_{3,12}=-\frac{2\sqrt{6}}{3}D_\eta$

$b^1_{4,4}=\frac{2}{15}(-2D_s-15D_q)-2B+7C+12\alpha$, $b^1_{4,5}=\frac{2\sqrt{15}}{15}(D_\xi+D_\eta)$, $b^1_{4,6}=-\frac{28}{15}D_s+12B$

$b^1_{4,7}=\frac{14\sqrt{15}}{15}D_\xi$, $b^1_{4,8}=-\frac{8\sqrt{3}}{15}D_t$, $b^1_{4,9}=\frac{2\sqrt{21}}{105}(-45D_\xi-52D_\eta)$, $b^1_{4,10}=\frac{4\sqrt{2}}{5}D_t$

$b^1_{4,11}=-\frac{2\sqrt{6}}{15}(5D_\xi-2D_\eta)$, $b^1_{4,12}=-\frac{4\sqrt{70}}{21}(D_s-3D_q)$

$b^1_{5,5}=\frac{1}{3}(7D_q-D_t)-2B+7C+12\alpha$, $b^1_{5,6}=\frac{14\sqrt{5}}{15}D_\xi$, $b^1_{5,7}=12B$

$b^1_{5,8}=\frac{2\sqrt{5}}{5}(3D_\xi-4D_\eta)$, $b^1_{5,9}=\frac{4\sqrt{35}}{35}(3D_s+5D_q+D_t)$, $b^1_{5,10}=\frac{2\sqrt{30}}{15}(3D_\xi-4D_\eta)$

$b^1_{5,11}=-\frac{2\sqrt{10}}{15}(3D_s+5D_q+D_t)$, $b^1_{5,12}=-\frac{2\sqrt{42}}{21}(D_\xi+8D_\eta)$

$b^1_{6,6}=\frac{1}{15}(-22D_s+45D_q)-8B+4C+12\alpha$, $b^1_{6,7}=\frac{\sqrt{15}}{15}(11D_\xi-3D_\eta)$, $b^1_{6,8}=\frac{\sqrt{3}}{15}D_t$

$b^1_{6,9}=\frac{\sqrt{21}}{105}(-15D_\xi+13D_\eta)$, $b^1_{6,10}=-\frac{3\sqrt{2}}{5}D_t$, $b^1_{6,11}=-\frac{\sqrt{6}}{15}(10D_\xi+3D_\eta)$

$b^1_{6,12}=-\frac{\sqrt{70}}{21}(4D_s+9D_q)$

$b^1_{7,7}=\frac{1}{2}(-7D_q+D_t)-8B+4C+12\alpha$, $b^1_{7,8}=\frac{\sqrt{5}}{5}(D_\xi+D_\eta)$, $b^1_{7,9}=\frac{\sqrt{35}}{70}(4D_s-5D_q-D_t)$

$b^1_{7,10}=\frac{2\sqrt{30}}{5}(D_\xi+D_\eta)$, $b^1_{7,11}=-\frac{\sqrt{10}}{10}(4D_s-5D_q-D_t)$, $b^1_{7,12}=-\frac{2\sqrt{42}}{21}(D_\xi-6D_\eta)$

$b^1_{8,8}=\frac{1}{5}(-2D_s-15D_q)-12B+4C+20\alpha$, $b^1_{8,9}=\frac{3\sqrt{7}}{35}(D_\xi+15D_\eta)$

$b^1_{8,10}=\frac{\sqrt{6}}{5}(-4D_s+5D_q)$, $b^1_{8,11}=-\frac{\sqrt{2}}{5}(-2D_\xi+5D_\eta)$, $b^1_{8,12}=-\frac{\sqrt{210}}{105}D_t$

$b^1_{9,9}=\frac{1}{70}(8D_s+165D_q+45D_t)-12B+4C+20\alpha$, $b^1_{9,10}=-\frac{2\sqrt{42}}{5}D_\xi$

$b^1_{9,11}=-\frac{\sqrt{14}}{70}(28D_s+35D_q-5D_t)$, $b^1_{9,12}=-\frac{2\sqrt{30}}{15}(3D_\xi-D_\eta)$

TABLE V. (*Continued*).

^3B_k	$^3P_1$	$^3P_2$	^3D	$^3F_1$	$^3F_1'$	$^3F_2$	$^3F_2'$	^3G	$^3G'$	^3H	$^3H'$	$^3H''$

$b^1_{10,10}=\frac{2}{5}(D_s-10D_q)-17B+4C+30\alpha$, $b^1_{10,11}=-\frac{2\sqrt{3}}{15}(3D_\xi+10D_\eta)$, $b^1_{10,12}=-\frac{4\sqrt{35}}{35}D_t$

$b^1_{11,11}=\frac{2}{15}(-3D_s-5D_q+5D_t)-17B+4C+30\alpha$, $b^1_{11,12}=\frac{2\sqrt{105}}{15}(D_\xi-2D_\eta)$

$b^1_{12,12}=\frac{2}{3}(-D_s+6D_q)-17B+4C+30\alpha$

$b^2_{1,1}=\frac{7}{15}(-D_s+3D_\xi)-7B+7C+2\alpha$, $b^2_{1,2}=\frac{2\sqrt{14}}{15}(D_s-3D_\xi)+4\sqrt{14}B$, $b^2_{1,3}=\frac{4\sqrt{105}}{15}(D_s+D_\xi)$

$b^2_{1,4}=\frac{1}{30}(-21D_s+15D_q-5D_t-24D_\xi-10D_\eta)$, $b^2_{1,5}=\frac{\sqrt{15}}{30}(-4D_s+5D_q+D_t+8D_\xi-6D_\eta)$

$b^2_{1,6}=\frac{1}{30}(-24D_s-75D_q+25D_t-48D_\xi+50D_\eta)$, $b^2_{1,7}=\frac{\sqrt{15}}{30}(-8D_s-25D_q-5D_t+16D_\xi+30D_\eta)$, $b^2_{1,8}=\frac{\sqrt{3}}{30}(-35D_q+D_t-14D_\eta)$

$b^2_{1,9}=\frac{\sqrt{21}}{30}(-5D_q-D_t-10D_\eta)$, $b^2_{1,10}=\frac{7\sqrt{6}}{30}(5D_q+D_t)$, $b^2_{1,11}=\frac{\sqrt{70}}{60}(15D_q-5D_t+8D_\eta)$, $b^2_{1,12}=\frac{\sqrt{2}}{20}(35D_q-D_t-56D_\eta)$

$b^2_{2,2}=\frac{133}{105}(D_s-3D_\xi)-3B+4C+2\alpha$, $b^2_{2,3}=\frac{4\sqrt{30}}{15}(D_s+D_\xi)$, $b^2_{2,4}=\frac{\sqrt{14}}{210}(-66D_s-75D_q+25D_t-132D_\xi+50D_\eta)$

$b^2_{2,5}=\frac{\sqrt{210}}{210}(-22D_s-25D_q-5D_t+44D_\xi+30D_\eta)$, $b^2_{2,6}=\frac{\sqrt{14}}{840}(-96D_s+15D_q-5D_t-192D_\xi-10D_\eta)$

$b^2_{2,7}=\frac{\sqrt{210}}{840}(-32D_s+5D_q+D_t+64D_\xi-6D_\eta)$, $b^2_{2,8}=\frac{17\sqrt{42}}{840}(35D_q-D_t+14D_\eta)$, $b^2_{2,9}=\frac{17\sqrt{6}}{120}(5D_q+D_t+10D_\eta)$

$b^2_{2,10}=-\frac{\sqrt{21}}{30}(5D_q+D_t)$, $b^2_{2,11}=\frac{\sqrt{5}}{60}(-15D_q+5D_t-8D_\eta)$, $b^2_{2,12}=\frac{\sqrt{7}}{140}(-35D_q+D_t+56D_\eta)$

$b^2_{3,3}=\frac{1}{21}(-3D_s+44D_q+9D_\xi+44D_\eta)-5B+4C+6\alpha$, $b^2_{3,4}=\frac{\sqrt{105}}{105}(-6D_s+25D_q+5D_t+24D_\xi+10D_\eta)$

$b^2_{3,5}=\frac{\sqrt{7}}{21}(-6D_s+25D_q-3D_t-14D_\eta)$, $b^2_{3,6}=\frac{\sqrt{105}}{140}(8D_s+25D_q+5D_t-32D_\xi+10D_\eta)$, $b^2_{3,7}=\frac{\sqrt{7}}{28}(8D_s+25D_q-3D_t-14D_\eta)$

$b^2_{3,8}=\frac{\sqrt{35}}{140}(-40D_s+15D_q+3D_t-42D_\eta)$, $b^2_{3,9}=\frac{\sqrt{5}}{140}(-40D_s+15D_q-21D_t-160D_\xi+78D_\eta)$, $b^2_{3,10}=\frac{\sqrt{70}}{210}(-35D_q+9D_t+28D_\eta)$

$b^2_{3,11}=\frac{\sqrt{6}}{12}(-5D_q-D_t+4D_\eta)$, $b^2_{3,12}=\frac{\sqrt{210}}{60}(-5D_q-D_t+4D_\eta)$

$b^2_{4,4}=\frac{1}{60}(8D_s-45D_q+15D_t+6D_\xi-120D_\eta)-2B+7C+12\alpha$, $b^2_{4,5}=\frac{\sqrt{15}}{60}(-4D_s+5D_q+D_t-2D_\xi-16D_\eta)$

$b^2_{4,6}=\frac{7}{30}(4D_s+3D_\xi)+12B$, $b^2_{4,7}=\frac{7\sqrt{15}}{30}(-2D_s-D_\xi)$, $b^2_{4,8}=\frac{\sqrt{3}}{30}(70D_s-2D_t+45D_\xi-32D_\eta)$

$b^2_{4,9}=\frac{\sqrt{21}}{210}(90D_s-130D_q-26D_t-45D_\xi-80D_\eta)$, $b^2_{4,10}=\frac{\sqrt{6}}{30}(10D_s+5D_q+D_t+20D_\xi+20D_\eta)$

$b^2_{4,11}=\frac{\sqrt{70}}{210}(20D_s+45D_q-15D_t-30D_\xi-51D_\eta)$, $b^2_{4,12}=\frac{\sqrt{2}}{10}(-35D_q+D_t-10D_\xi+11D_\eta)$

$b^2_{5,5}=\frac{1}{12}(-7D_q-3D_t-6D_\xi+8D_\eta)-2B+7C+12\alpha$, $b^2_{5,6}=\frac{7\sqrt{15}}{30}(-2D_s-D_\xi)$, $b^2_{5,7}=-\frac{7}{2}D_\xi+12B$

$b^2_{5,8}=\frac{\sqrt{5}}{10}(6D_s+10D_q+2D_t+9D_\xi+16D_\eta)$, $b^2_{5,9}=\frac{\sqrt{35}}{70}(-12D_s+50D_q-6D_t-21D_\xi)$

TABLE V. (*Continued*).

^3B_k	$^3P_1$	$^3P_2$	^3D	$^3F_1$	$^3F_1'$	$^3F_2$	$^3F_2'$	^3G	$^3G'$	^3H	$^3H'$	$^3H''$

$b^2_{5,10}=\frac{\sqrt{10}}{30}(6D_s-25D_q+3D_t-12D_\xi-40D_\eta)$, $b^2_{5,11}=\frac{\sqrt{42}}{42}(2D_s-20D_q-4D_t+10D_\xi-11D_\eta)$

$b^2_{5,12}=\frac{\sqrt{30}}{30}(6D_s+10D_q+2D_t-6D_\xi+D_\eta)$

$b^2_{6,6}=\frac{1}{20}(88D_s+135D_q-45D_t+66D_\xi+360D_\eta)-8B+4C+12\alpha$, $b^2_{6,7}=\frac{\sqrt{15}}{120}(-44D_s-15D_q-3D_t-22D_\xi+48D_\eta)$

$b^2_{6,8}=\frac{\sqrt{3}}{120}(-35D_q+D_t+30D_\xi+16D_\eta)$, $b^2_{6,9}=\frac{\sqrt{21}}{840}(60D_s+65D_q+13D_t-30D_\xi+40D_\eta)$

$b^2_{6,10}=\frac{\sqrt{6}}{120}(40D_s-15D_q-3D_t+80D_\xi-60D_\eta)$, $b^2_{6,11}=\frac{\sqrt{70}}{840}(80D_s-135D_q+45D_t-120D_\xi+153D_\eta)$

$b^2_{6,12}=\frac{\sqrt{2}}{40}(105D_q-3D_t-40D_\xi-33D_\eta)$

$b^2_{7,7}=\frac{1}{8}(7D_q+3D_t-22D_\xi-8D_\eta)-8B+4C+12\alpha$, $b^2_{7,8}=\frac{\sqrt{5}}{40}(4D_s-5D_q-D_t+6D_\xi-8D_\eta)$

$b^2_{7,9}=\frac{\sqrt{35}}{280}(-8D_s-25D_q+3D_t-14D_\xi)$, $b^2_{7,10}=\frac{\sqrt{10}}{40}(8D_s+25D_q-3D_t-16D_\xi+40D_\eta)$

$b^2_{7,11}=\frac{\sqrt{42}}{168}(8D_s+60D_q+12D_t+40D_\xi+33D_\eta)$, $b^2_{7,12}=\frac{\sqrt{30}}{40}(8D_s-10D_q-2D_t-8D_\xi-D_\eta)$

$b^2_{8,8}=\frac{1}{40}(8D_s-45D_q+15D_t-6D_\xi+120D_\eta)-12B+4C+20\alpha$, $b^2_{8,9}=\frac{3\sqrt{7}}{280}(4D_s-75D_q-15D_t-14D_\xi)$

$b^2_{8,10}=\frac{\sqrt{2}}{40}(8D_s+25D_q+5D_t-48D_\xi-20D_\eta)$, $b^2_{8,11}=\frac{\sqrt{210}}{840}(35D_q-D_t-168D_\xi-7D_\eta)$

$b^2_{8,12}=\frac{\sqrt{6}}{40}(16D_s+15D_q-5D_t+8D_\xi+15D_\eta)$

$b^2_{9,9}=\frac{1}{280}(-16D_s+1035D_q-105D_t-78D_\xi-120D_\eta)-12B+4C+20\alpha$, $b^2_{9,10}=\frac{\sqrt{14}}{280}(56D_s+35D_q+15D_t-112D_\xi)$

$b^2_{9,11}=\frac{\sqrt{30}}{120}(24D_s+10D_q+2D_t+24D_\xi-43D_\eta)$, $b^2_{9,12}=\frac{\sqrt{42}}{40}(-8D_s+8D_\xi-5D_\eta)$

$b^2_{10,10}=\frac{1}{60}(12D_s+160D_q+6D_\xi+160D_\eta)-17B+4C+30\alpha$, $b^2_{10,11}=\frac{\sqrt{105}}{60}(-4D_s-10D_q-2D_t+D_t+D_\xi+8D_\eta)$

$b^2_{10,12}=\frac{\sqrt{3}}{60}(-12D_s+50D_q+10D_t-33D_\xi-40D_\eta)$

$b^2_{11,11}=\frac{1}{24}(8D_s+36D_q-12D_t-3D_\xi-48D_\eta)-17B+4C+30\alpha$, $b^2_{11,12}=\frac{\sqrt{35}}{280}(140D_q-4D_t-7D_\xi+112D_\eta)$

$b^2_{12,12}=\frac{1}{40}(-8D_s-60D_q+20D_t-39D_\xi+80D_\eta)-17B+4C+30\alpha$

$b^3_{1,1}=\frac{7}{15}(-D_s-3D_\xi)-7B+7C+2\alpha$, $b^3_{1,2}=\frac{2\sqrt{14}}{15}(D_s+3D_\xi)+4\sqrt{14}B$, $b^3_{1,3}=\frac{4\sqrt{105}}{15}(D_s-D_\xi)$

TABLE V. (*Continued*).

^3B_k	$^3P_1$	$^3P_2$	^3D	$^3F_1$	$^3F_1'$	$^3F_2$	$^3F_2'$	^3G	$^3G'$	^3H	$^3H'$	$^3H''$

$b^3_{1,4}=\frac{1}{30}(-12D_s+15D_q-5D_t+24D_\xi+10_\eta)$, $b^3_{1,5}=\frac{\sqrt{15}}{30}(-4D_s+5D_q+D_t-8D_\xi+6D_\eta)$

$b^3_{1,6}=\frac{1}{30}(-24D_s-75D_q+25D_t-48D_\xi-50D_\eta)$, $b^3_{1,7}=\frac{\sqrt{15}}{30}(-8D_s-25D_q-5D_t-16D_\xi-30D_\eta)$, $b^3_{1,8}=\frac{\sqrt{3}}{30}(-35D_q+D_t+14D_\eta)$

$b^3_{1,9}=\frac{\sqrt{21}}{30}(-5D_q-D_t+10D_\eta)$, $b^3_{1,10}=\frac{7\sqrt{6}}{30}(5D_q+D_t)$, $b^3_{1,11}=\frac{\sqrt{70}}{60}(15D_q-5D_t-8D_\eta)$, $b^3_{1,12}=\frac{\sqrt{2}}{20}(35D_q-D_t+56D_\eta)$

$b^3_{2,2}=\frac{133}{105}(D_s+3D_\xi)-3B+4C+2\alpha$, $b^3_{2,3}=\frac{4\sqrt{30}}{15}(D_s-D_\xi)$, $b^3_{2,4}=\frac{\sqrt{14}}{210}(-66D_s-75D_q+25D_t+132D_\xi-50D_\eta)$

$b^3_{2,5}=\frac{\sqrt{210}}{210}(-22D_s-25D_q-5D_t-44D_\xi-30D_\eta)$, $b^3_{2,6}=\frac{\sqrt{14}}{840}(-96D_s+15D_q-5D_t+192D_\xi+10D_\eta)$

$b^3_{2,7}=\frac{\sqrt{210}}{840}(-32D_s+5D_q+D_t-64D_\xi+6D_\eta)$, $b^3_{2,8}=\frac{17\sqrt{42}}{840}(35D_q-D_t-14D_\eta)$, $b^3_{2,9}=\frac{17\sqrt{6}}{120}(5D_q+D_t-10D_\eta)$

$b^3_{2,10}=\frac{\sqrt{21}}{30}(-5D_q-D_t)$, $b^3_{2,11}=\frac{\sqrt{5}}{60}(-15D_q+5D_t+8D_\eta)$, $b^3_{2,12}=\frac{\sqrt{7}}{140}(-35D_q+D_t-56D_\eta)$

$b^3_{3,3}=\frac{1}{21}(-3D_s+44D_q-9D_\xi-44D_\eta)-5B+4C+6\alpha$, $b^3_{3,4}=\frac{\sqrt{105}}{105}(-6D_s+25D_q+5D_t-24D_\xi-10D_\eta)$

$b^3_{3,5}=\frac{\sqrt{7}}{21}(-6D_s+25D_q-3D_t+14D_\eta)$, $b^3_{3,6}=\frac{\sqrt{105}}{140}(8D_s+25D_q+5D_t+32D_\xi-10D_\eta)$, $b^3_{3,7}=\frac{\sqrt{7}}{28}(8D_s+25D_q-3D_t+14D_\eta)$

$b^3_{3,8}=\frac{\sqrt{35}}{140}(-40D_s+15D_q+3D_t+42D_\eta)$, $b^3_{3,9}=\frac{\sqrt{5}}{140}(-40D_s+15D_q-21D_t+160D_\xi-78D_\eta)$, $b^3_{3,10}=\frac{\sqrt{70}}{210}(-35D_q+9D_t-28D_\eta)$

$b^3_{3,11}=\frac{\sqrt{6}}{12}(-5D_q-D_t-4D_\eta)$, $b^3_{3,12}=\frac{\sqrt{210}}{60}(-5D_q-D_t-4D_\eta)$

$b^3_{4,4}=\frac{1}{60}(8D_s-45D_q+15D_t-6D_\xi+120D_\eta)-2B+7C+12\alpha$, $b^3_{4,5}=\frac{\sqrt{15}}{60}(-4D_s+5D_q+D_t+2D_\xi+16D_\eta)$

$b^3_{4,6}=\frac{7}{30}(4D_s-3D_\xi)+12B$, $b^3_{4,7}=\frac{7\sqrt{15}}{30}(-2D_s+D_\xi)$, $b^3_{4,8}=\frac{\sqrt{3}}{30}(70D_q-2D_t-45D_\xi+32D_\eta)$

$b^3_{4,9}=\frac{\sqrt{21}}{210}(90D_s-130D_q-26D_t+45D_\xi+80D_\eta)$, $b^3_{4,10}=\frac{\sqrt{6}}{30}(10D_s+5D_q+D_t-20D_\xi-20D_\eta)$

$b^3_{4,11}=\frac{\sqrt{70}}{210}(20D_s+45D_q-15D_t+30D_\xi+51D_\eta)$, $b^3_{4,12}=\frac{\sqrt{2}}{10}(-35D_q+D_t+10D_\xi-11D_\eta)$

$b^3_{5,5}=\frac{1}{12}(-7D_q-3D_t+6D_\xi-8D_\eta)-2B+7C+12\alpha$, $b^3_{5,6}=\frac{7\sqrt{15}}{30}(-2D_s+D_\xi)$, $b^3_{5,7}=\frac{7}{2}D_\xi+12B$

$b^3_{5,8}=\frac{\sqrt{5}}{10}(6D_s+10D_q+2D_t-9D_\xi-16D_\eta)$, $b^3_{5,9}=\frac{\sqrt{35}}{70}(-12D_s+50D_q-6D_t+21D_\xi)$

$b^3_{5,10}=\frac{\sqrt{10}}{30}(6D_s-25D_q+3D_t+12D_\xi+40D_\eta)$, $b^3_{5,11}=\frac{\sqrt{42}}{42}(2D_s-20D_q-4D_t-10D_\xi+11D_\eta)$

$b^3_{5,12}=\frac{\sqrt{30}}{30}(6D_s+10D_q+2D_t+6D_\xi-D_\eta)$

$b^3_{6,6}=\frac{1}{120}(88D_s+135D_q-45D_t-66D_\xi-360D_\eta)-8B+4C+12\alpha$, $b^3_{6,7}=\frac{\sqrt{15}}{120}(-44D_s-15D_q-3D_t+22D_\xi-48D_\eta)$

TABLE V. (*Continued*).

^3B_k	$^3P_1$	$^3P_2$	^3D	$^3F_1$	$^3F_1'$	$^3F_2$	$^3F_2'$	^3G	$^3G'$	^3H	$^3H'$	$^3H''$

$b^3_{6,8}=\frac{\sqrt{3}}{120}(-35D_q+D_t-30D_\xi-16D_\eta)$, $b^3_{6,9}=\frac{\sqrt{21}}{840}(60D_s+65D_q+13D_t+30D_\xi-40D_\eta)$

$b^3_{6,10}=\frac{\sqrt{6}}{120}(40D_s-15D_q-3D_t-80D_\xi+60D_\eta)$, $b^3_{6,11}=\frac{\sqrt{70}}{840}(80D_s-135D_q+45D_t+120D_\xi-153D_\eta)$

$b^3_{6,12}=\frac{\sqrt{2}}{40}(105D_q-3D_t+40D_\xi+33D_\eta)$

$b^3_{7,7}=\frac{1}{8}(7D_q+3D_t+22D_\xi+8D_\eta)-8B+4C+12\alpha$, $b^3_{7,8}=\frac{\sqrt{5}}{40}(4D_s-5D_q-D_t-6D_\xi+8D_\eta)$

$b^3_{7,9}=\frac{\sqrt{35}}{280}(-8D_s-25D_q+3D_t+14D_\xi)$, $b^3_{7,10}=\frac{\sqrt{10}}{40}(8D_s+25D_q-3D_t+16D_\xi-40D_\eta)$

$b^3_{7,11}=\frac{\sqrt{42}}{168}(8D_s+60D_q+12D_t-40D_\xi-33D_\eta)$, $b^3_{7,12}=\frac{\sqrt{30}}{40}(8D_s-10D_q-2D_t+8D_\xi+D_\eta)$

$b^3_{8,8}=\frac{1}{40}(8D_s-45D_q+15D_t+6D_\xi-120D_\eta)-12B+4C+20\alpha$, $b^3_{8,9}=\frac{3\sqrt{7}}{280}(4D_s-75D_q-15D_t+14D_\xi)$

$b^3_{8,10}=\frac{\sqrt{2}}{40}(8D_s+25D_q+5D_t+48D_\xi+20D_\eta)$, $b^3_{8,11}=\frac{\sqrt{210}}{840}(35D_q-D_t+168D_\xi+7D_\eta)$

$b^3_{8,12}=\frac{\sqrt{6}}{40}(16D_s+15D_q-5D_t-8D_\xi-15D_\eta)$

$b^3_{9,9}=\frac{1}{280}(-16D_s+1035D_q-105D_t+78D_\xi+120D_\eta)-12B+4C+20\alpha$, $b^3_{9,10}=\frac{\sqrt{14}}{280}(56D_s+35D_q+15D_t+112D_\xi)$

$b^3_{9,11}=\frac{\sqrt{30}}{120}(24D_s+10D_q+2D_t-24D_\xi+43D_\eta)$, $b^3_{9,12}=\frac{\sqrt{42}}{40}(-8D_s-8D_\xi+5D_\eta)$

$b^3_{10,10}=\frac{1}{60}(12D_s+160D_q-6D_\xi-160D_\eta)-17B+4C+30\alpha$, $b^3_{10,11}=\frac{\sqrt{105}}{60}(-4D_s-10D_q-2D_t-D_\xi-8D_\eta)$

$b^3_{10,12}=\frac{\sqrt{3}}{60}(-12D_s+50D_q+10D_t+33D_\xi+40D_\eta)$

$b^3_{11,11}=\frac{1}{24}(8D_s+36D_q-12D_t+3D_\xi+48D_\eta)-17B+4C+30\alpha$, $b^3_{11,12}=\frac{\sqrt{35}}{280}(140D_q-4D_t+7D_\xi-112D_\eta)$

$b^3_{12,12}=\frac{1}{40}(-8D_s-60D_q+20D_t+39D_\xi-80D_\eta)-17B+4C+30\alpha$

give these energy matrices obtained with the weak-field approximation scheme.

The definitions of crystal-field parameters are

$$D_s=-\tfrac{2}{7}eq\,\beta\frac{1}{R_A^3}\langle r^2\rangle,\quad D_q=\tfrac{1}{42}eq\,\alpha\frac{1}{R_A^5}\langle r^4\rangle,$$

$$D_t=\tfrac{5}{6}eq\,\nu\frac{1}{R_A^5}\langle r^4\rangle,\quad D_\xi=\tfrac{2}{7}eq\,\epsilon\frac{1}{R_A^3}\langle r^2\rangle,$$

$$D_\eta=-\tfrac{5}{42}eq\,\delta\frac{1}{R_A^5}\langle r^4\rangle.$$

The single-electron matrix elements are

$$\langle\pm2|\hat{V}|\pm2\rangle=2D_s+D_q,\quad \langle\pm1|\hat{V}|\pm1\rangle=-D_s-4D_q,$$

$$\langle\pm2|\hat{V}|\mp2\rangle=D_t,\quad \langle\pm1|\hat{V}|\mp1\rangle=-3D_\xi+4D_\eta,$$

$$\langle\pm2|\hat{V}|\pm1\rangle=0,\quad \langle\pm1|\hat{V}|0\rangle=0,\quad \langle\pm2|\hat{V}|\mp1\rangle=0,$$

$$\langle0|\hat{V}|0\rangle=-2D_s+6D_q,\quad \langle\pm2|\hat{V}|0\rangle=-\sqrt{6}(D_\xi+D_\eta).$$

The basis functions of irreducible representations of D_2 point-group symmetry are given in Table III. The functions are all of the form $|L,M_L\rangle$.

The quintet energy matrix elements are

$$\left\langle {}^5B_1({}^5D)\left|\sum \hat{V}\right|{}^5B_1({}^5D)\right\rangle = -2D_s - D_q + Dt \ ,$$

$$\left\langle {}^5B_2({}^5D)\left|\sum \hat{V}\right|{}^5B_2({}^5D)\right\rangle = D_s + 4D_q - 3D_\xi + 4D_\eta \ ,$$

$$\left\langle {}^5B_3({}^5D)\left|\sum \hat{V}\right|{}^5B_3({}^5D)\right\rangle = D_s + 4D_q + 3D_\xi - 4D_\eta \ ,$$

$^5A_1$	^5D	$^5D'$
	$-2D_s - D_q - D_t$	$2\sqrt{3}(D_\xi + D_\eta)$
		$2D_s - 6D_q$

The triplet energy matrices are given in Tables IV and V.

[1]R. K. Moore and W. B. White, Can. Mineral. **11**, 791 (1972).
[2]R. G. Burns, *Mineralogical Applications of Crystal Field Theory* (Cambridge University Press, Cambridge, England, 1970).
[3]P. G. Manning, Can. Mineral. **9**, 237 (1967).
[4]G. A. Slack and R. M. Chrenko, J. Opt. Soc. Am. **61**, 1325 (1971).
[5]Lin Chuanyi, Bull. Mineral. **104**, 218 (1981).
[6]D. J. Newman, D. C. Price, and W. A. Runciman, Am. Mineral. **63**, 1278 (1978).
[7]M. G. Zhao and M. L. Du, Phys. Rev. B **28**, 6481 (1983).
[8]F. E. Huggins, Am. Mineral. **60**, 316 (1975).
[9]G. A. Novak and G. V. Gibbs, Am. Mineral. **56**, 791 (1971).
[10]W. A. Runciman and D. Sengupta, Am. Mineral. **59**, 563 (1974).
[11]D. J. Newman and W. Urban, Adv. Phys. **24**, 793 (1975).
[12]W. B. White and R. K. Moore, Am. Mineral. **57**, 1692 (1972).
[13]M. G. Zhao, J. A. Xu, and G. L. Bai, J. Phys. C **13**, 5959 (1982).
[14]M. G. Zaho, J. A. Xu, and G. L. Bai, Phys. Rev. B **27**, 1516 (1983).
[15]D. J. Newman, Adv. Phys. **20**, 197 (1971).
[16]D. J. Newman and S. C. Chen, Phys. Rev. B **25**, 41 (1982).
[17]G. Amthauer, H. Annersten, and S. S. Hafner, Z. Kristallogr. **143**, 14 (1976).