

AM-76-035

D. S. Goldman and G. R. Rossman

The spectra of iron in orthopyroxene revisited: the splitting of the
 $^5t_{2g}$ ground state

Supplement: The point-charge model

American Mineralogist, 62, pages 151-157

The Spectra of Iron in Orthopyroxene Revisited:
The Splitting of the ${}^5T_{2g}$ Ground State

D. S. Goldman and G. R. Rossman

2469
~~2469~~
revised
for
microfilm

Supplement:

THE POINT-CHARGE MODEL

Introduction

The operator-equivalent point-charge method used to derive energy expressions for specified crystal-field states in the analysis of electronic absorption spectra is described in detail in Hutchings (1964). Hutchings includes the necessary formulas to derive the crystal-field potential and to rewrite it in terms of the operator equivalents. Extensive tables are presented that contain the various matrix elements of the operator equivalents for coupled wavefunctions so that expressions for the crystal-field states can be determined. The operator-equivalent method, as applied to the spectra of Fe^{2+} in the M(2) site of orthopyroxene by Goldman and Rossman (1976), will now be outlined. It is hoped that the reader will gain sufficient familiarity with the procedural aspects of this method so that it could be applied to spectra arising from a variety of coordination geometries.

THE CRYSTAL-FIELD POTENTIAL

The general expression for the crystal-field potential in terms of spherical harmonics at point (r, θ, ϕ) is

$$V(r, \theta, \phi) = \sum_{n=0}^{\infty} \cdot \sum_{m=-n}^n r^n Y'_{nm} Y_n^m(\theta, \phi) \quad (1)$$

where

$$Y'_{nm} = \sum_j \frac{4\pi}{(2n+1)} \frac{q_j}{R_j^{n+1}} (-1)^m Y_n^{-m}(\theta_j, \phi_j). \quad (2)$$

Therefore, Y'_{nm} results from a summation of harmonic contributions from all j point charges in the coordination site.

Figure 1 represents the idealized geometry of a C_{2v} coordination site containing a dihedral two-fold rotation axis. Z coincides with the two-fold axis of the site and the two mirror planes are located in XZ and YZ and are mutually orthogonal. In equation 2, θ is the angular measure of point j from Z and ϕ is the angular measure of point j from X about Z . Hence, points 1 through 6 have (r, θ, ϕ) coordinates (a_1, θ_1, π) , $(a_1, \theta_1, 0)$, (a_2, θ_2, π) , $(a_2, \theta_2, 0)$, $(a_3, \theta_3, \frac{\pi}{2})$ and $(a_3, \theta_3, \frac{3\pi}{2})$, respectively.

The derivation of the Y_2^0 spherical harmonic contribution to the crystal-field potential serves to illustrate the procedure to derive the remaining terms. Given that (Hutchings, 1964, table 3)

$$Y_2^0 = \frac{1}{4} \left(\frac{5}{\pi} \right)^{\frac{1}{2}} (3 \cos^2 \theta - 1)$$

and assuming that each point contributes the same charge, q , equation 2 over all six points in figure 1 becomes

$$Y'_{20} = \left(\frac{\pi}{5} \right)^{\frac{1}{2}} q \sum_j \left(\frac{3 \cos^2 \theta_j - 1}{a_j^3} \right) \quad (3)$$

Substituting Y'_{20} into equation 1, the contribution to the potential from Y_2^0 is

$$v_{20} = \left(\frac{\pi}{5} \right)^{\frac{1}{2}} q r^2 \left[\sum_j \frac{(3 \cos^2 \theta_j - 1)}{a_j^3} \right] Y_2^0 \quad (4)$$

In this way, the remaining terms in the potential are derived. Excluding harmonic terms with $n > 4$ (Figgis, 1966, p. 32), contributions from the Y_2^0 , $Y_2^{\pm 2}$, Y_4^0 , $Y_4^{\pm 2}$ and $Y_4^{\pm 4}$ harmonic terms occur in this potential.

The potential is now rewritten in terms of the operator equivalents. The operators that are formed, which operate on the angular part of the wavefunctions, possess the same transformation properties under rotation as the potential. Hence, they allow for the matrix elements of the crystal-field potential between coupled wavefunctions that are specified by one particular value of angular momentum (LL_z) to be evaluated. Rewriting Y_2^0 in cartesian coordinates brings

$$Y_2^0 = \frac{1}{4} \left(\frac{5}{\pi} \right)^{\frac{1}{2}} \left(\frac{3z^2 - r^2}{r^2} \right)$$

In operator equivalents, Y_2^0 becomes (Hutchings, 1964, table 8)

$$Y_2^0 = \frac{1}{4r^2} \left(\frac{5}{\pi} \right)^{\frac{1}{2}} \alpha_J \langle r^2 \rangle [3L_z^2 - L(L+1)] = \frac{1}{4r^2} \left(\frac{5}{\pi} \right)^{\frac{1}{2}} \alpha_J \langle r^2 \rangle O_2^0 \quad (5)$$

where α_J is a constant multiplicative factor which is equal to $-\frac{2}{21}$ for $3d^6$ ions such as Fe^{2+} (Hutchings, 1964, table 7), and O_2^0 is the standard notation for the operator equivalent of Y_2^0 . Substituting equation 5 into equation 4 brings

$$V_{20} = -\frac{1}{42} q \langle r^2 \rangle \left[\sum_j \frac{(3\cos^2\theta_j - 1)}{a_j^3} \right] O_2^0 \quad (6)$$

Continuing for the remaining terms, the potential is then entirely rewritten using the operator equivalents.

In C_{2v} symmetry with Z as a dihedral axis, three electronic transitions are allowed; $A_1 \rightarrow A_1$, $A_1 \rightarrow B_1$ and $A_1 \rightarrow B_2$. Hence, spectral analysis provides three parameters whereas five coefficients occur in the potential. After subtracting

the octahedral terms from the potential in order to solve for $\Delta (=10 Dq)$, the five coefficients that still remain are reduced to two by rewriting each a_j in terms of \bar{a} , the average metal-ligand bond distance (or any other specified distance). For O_2^0 , equation 6 becomes

$$v_{20} = -\frac{1}{42} \frac{q \langle r^2 \rangle}{\bar{a}^3} \left[\sum_j \left(\frac{3 \cos^2 \theta_j - 1}{(a_j / \bar{a})^3} \right) - v_{20}^{\text{oct}} \right] O_2^0 \quad (7)$$

Since $a_1 = a_2 = a_3 = \bar{a}$, $\theta_1 = \theta_2 = \frac{\pi}{4}$, $\theta_3 = \theta_4 = \frac{3\pi}{4}$, and $\theta_5 = \theta_6 = \frac{\pi}{2}$ in octahedral geometry (figure 1), the summation in equation 6 over all six points is zero, and $v_{20}^{\text{oct}} = 0$. Hence, there are no octahedral contributions to be extracted from v_{20} and the summation in equation 7 within the brackets results in a numerical value for the A coefficient used in Goldman and Rossman (1976). Similarly, the remaining terms in the potential are:

$$(v_2^2 + v_2^{-2}) = -\frac{1}{14} \frac{q \langle r^2 \rangle}{\bar{a}^3} \left[\sum_j \left(\frac{\sin^2 \theta_j \cos^2 \phi_j - \sin^2 \theta_j \sin^2 \phi_j}{(a_j / \bar{a})^3} \right) \right] O_2^2 \quad (8)$$

$$v_4^0 = \frac{1}{4032} \frac{q \langle r^4 \rangle}{\bar{a}^5} \left[\sum_j 2 \cdot \left(\frac{35 \cos^4 \theta_j - 30 \cos^2 \theta_j + 3}{(a_j / \bar{a})^5} \right) + 14 \right] O_4^0 \quad (9)$$

$$(v_4^2 + v_4^{-2}) = \frac{5}{504} \frac{q \langle r^4 \rangle}{\bar{a}^5} \left[\sum_j \frac{(\sin^2 \theta_j \cos^2 \phi_j - \sin^2 \theta_j \sin^2 \phi_j) (7 \cos^2 \theta_j - 1)}{(a_j / \bar{a})^5} - 7 \right] O_4^2 \quad (10)$$

$$(v_4^4 + v_4^{-4}) = \frac{35}{2016} \frac{q \langle r^4 \rangle}{\bar{a}^5} \left[\sum_j \left(\frac{\sin^4 \theta_j \cos^4 \phi_j + \sin^4 \theta_j \sin^4 \phi_j}{(a_j / \bar{a})^5} \right) - 3 \right] O_4^4 \quad (11)$$

where the numerical values of the bracketed terms in equations 8 through 11 are the B through E coefficients in Goldman and Rossman (1976), respectively.

Certain terms that occur in the general expressions for the B, D and E coefficients are zero in C_{2v} symmetry and these terms have been omitted.

Because of the presence of mirror planes in XZ and YZ in Figure 1, bond distances from the metal ion to points 1 and 2 are identical (as are the distances to points 3 and 4, and 5 and 6). However, the crystallographic point-group symmetry of the M(2) coordination site in orthopyroxene is C_1 in which there are six unequal metal-oxygen bond distances. To conform to a C_{2v} symmetry with Z along the bisector of the O(3)-M(2)-O(6) angle, the averages of the bond lengths from M(2) to O(6) and O(3), O(1) and O(4), and O(2) and O(5) are used as a_1, a_2 and a_3 which have values of 2.462Å, 2.147Å and 2.052Å, respectively. \bar{a} has a value of 2.220Å (Ghose, 1965). Because the O(6)-M(2)-O(3) angle is 72.2° and the O(1)-M(2)-O(4) angle is 83°, θ_1 and θ_2 (Figure 1) are 36.1° and 138.5°, respectively. θ_3 is set at 90°. Using these values for θ_j and a_j and the values for ϕ_j shown in Figure 1, the coefficients A, B, C, D and E, calculated from equations 7 through 11, are 0.38066, -1.05474, 14.5148, 0.48616 and 0.56845, respectively.

The C_{2v} potential is written by defining two parameters

$$M = - \frac{1}{14} \frac{q \langle r^2 \rangle}{\bar{a}^3} \quad \text{and} \quad N = \frac{1}{504} \frac{q \langle r^4 \rangle}{\bar{a}^5},$$

and substituting A, B, C, D and E for the bracketed terms in equations 7 through 11, respectively. The potential, V, consists of an octahedral portion, and

$$M \left[\frac{A}{3} O_2^0 + B O_2^2 \right] + N \left[\frac{C}{8} O_4^0 + 5 D O_4^2 + \frac{35}{4} E O_4^4 \right] \quad (12)$$

Hence, there are three parameters, Δ , M and N, to be fitted from the spectra.

d - ORBITAL WAVEFUNCTIONS

Using the octahedral form of the C_{2v} potential

$$V^{\text{oct}'} = \frac{q \langle r^4 \rangle}{8a^5} \left[-\frac{1}{36} O_4^0 + \frac{5}{9} O_4^2 + \frac{5}{12} O_4^4 \right],$$

the five linear combinations of the d orbitals that transform as A_1, A_2, B_2, B_1 and A_1 in the C_{2v} symmetry group are found. This involves determining the elements of the 5×5 matrix of d orbitals. For instance, neglecting the common factor $(5/4\pi)^{1/2}$, the matrix element for $\langle Y_2^0 | V^{\text{oct}'} | Y_2^0 \rangle$ is found using Hutchings (1964, table 9). In this case, $L=2$ and $L_z=0$. Letting $\frac{q \langle r^4 \rangle}{8a^5} = \delta$ in $V^{\text{oct}'}$, table 9 in Hutchings (1964) indicates that

$$-\frac{1}{36} \delta \langle 0 | O_4^0 | 0 \rangle = \left(-\frac{1}{36} \delta\right) (72) = -2\delta$$

$$\frac{5}{9} \delta \langle 0 | O_4^2 | 0 \rangle = \left(\frac{5}{9} \delta\right) (0) = 0$$

$$\frac{5}{12} \delta \langle 0 | O_4^4 | 0 \rangle = \left(\frac{5}{12} \delta\right) (0) = 0$$

so that the matrix element for $\langle Y_2^0 | V^{\text{oct}'} | Y_2^0 \rangle$ is -2δ . Upon determining the remaining matrix elements, it is found that Y_2^0, Y_2^2 and Y_2^{-2} and Y_2^1 and Y_2^{-1} mix. The appropriate linear combinations are then determined in the conventional manner (Ballhausen, 1962) and the following wavefunctions are obtained:

$$d_{y^2} = \frac{1}{2}(2y^2 - x^2 - z^2) = -\frac{1}{2}Y_2^0 - \frac{1}{2}\sqrt{\frac{5}{2}}(Y_2^2 + Y_2^{-2})$$

$$d_{xz} = \sqrt{3}xz = \frac{1}{\sqrt{2}}(Y_2^1 - Y_2^{-1})$$

$$d_{yz} = \sqrt{3}yz = \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1})$$

$$d_{xy} = \sqrt{3}xy = \frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2})$$

$$d_{x^2-y^2} = \frac{\sqrt{3}}{2}(x^2 - y^2) = -\frac{\sqrt{3}}{2}Y_2^0 + \frac{1}{2}\sqrt{\frac{5}{2}}(Y_2^2 + Y_2^{-2})$$

which transform as A_1, B_1, B_2, A_2 and A_1 , respectively, in C_{2v} symmetry. Applying V^{oct} to the above wavefunctions remembering that $\delta = 0.75\Delta$ (Figgis, 1966, page 35), the energy of d_{y^2} and d_{xz} is 0.6Δ and the energy of d_{xy} , d_{yz} and $d_{x^2-y^2}$ is -0.4Δ . Therefore, d_{y^2} (A_1) and d_{xz} (B_1) arise from the splitting of the octahedral 5E_g state of Fe^{2+} as is indicated in the correlation tables for $C_{2v}(C_2)$ in Wilson, Decius and Cross (1955).

ENERGY EXPRESSIONS

The energy expressions for the five d wavefunctions in C_{2v} symmetry are found by applying the C_{2v} potential in equation 12 to each one of the wavefunctions using table 9 in Hutchings to evaluate the matrix elements. The expression for the A_2 state is

$$\begin{aligned} & \frac{1}{2} \langle Y_2^2 - Y_2^{-2} | V | Y_2^2 - Y_2^{-2} \rangle \\ &= \langle Y_2^2 | V | Y_2^2 \rangle - \langle Y_2^2 | V | Y_2^{-2} \rangle \\ &= \langle Y_2^{-2} | V | Y_2^{-2} \rangle - \langle Y_2^{-2} | V | Y_2^2 \rangle \end{aligned}$$

Taking the first term

$$\langle 1 | \frac{MA}{3} O_2^0 | 2 \rangle = \frac{MA}{3}(6) = 2MA$$

$$\langle 2 | MBO_2^2 | 2 \rangle = MB(0) = 0$$

$$-\langle 2 | \frac{MA}{3} O_2^0 | -2 \rangle = \frac{MA}{3}(0) = 0$$

$$-\langle 2 | MBO_2^2 | -2 \rangle = -MB(0) = 0$$

and the second term

$$\langle 2 | \frac{NC}{8} O_4^0 | 2 \rangle = \frac{NC}{8}(12) = \frac{3}{2}NC$$

$$\langle 2 | 5NDO_4^2 | 2 \rangle = 5ND(0) = 0$$

$$\langle 2 | \frac{35}{4} NEO_4^4 | 2 \rangle = \frac{35}{4}NE(0) = 0$$

$$-\langle 2 | \frac{NC}{8} O_4^0 | -2 \rangle = \frac{NC}{8}(0) = 0$$

$$-\langle 2 | 5NDO_4^2 | -2 \rangle = 5ND(0) = 0$$

$$-\langle 2 | \frac{35}{4} NEO_4^4 | -2 \rangle = \frac{35}{4}NE(12) = -105NE$$

and remembering that $\langle d_{xy} | V^{oct} | d_{xy} \rangle = -0.4\Delta$, the entire energy expression for the A_2 state is

$$2MA + \frac{3}{2}NC - 105NE - 0.4\Delta$$

which is given in Goldman and Rossman (1976, table 2). In this way, energy expressions for the remaining four states are determined.

Since the two A_1 states have the same transformational symmetry, they can mutually interact. To account for this configurational interaction, a 2x2 matrix is formed for d_{y^2} and $d_{x^2-z^2}$. The two eigenvalues of this configuration interaction matrix are the resulting energies of the two A_1 states. The energy expression for the two A_1 states derived from the configuration interaction matrix is

$$\begin{aligned} & \left[\frac{9}{16}(3C+40D+70E) + \frac{3}{15}(19C-120D+70E) \right] N + 0.1\Delta + \\ & \left\{ \frac{1}{4} \Delta^2 + [(A+3B)^2 + 3(B-A)^2] M^2 - \left[\frac{3}{8}(19C-120D+70E)(A+3B) \right. \right. \\ & \left. \left. - \frac{9}{8}(3C+40D+70E)(A+3B) - \frac{45}{4}(C+8D-14E)(B-A) \right] M \cdot N \right. \\ & \left. + \left[\frac{9}{256}(19C-120D+70E)^2 + \frac{81}{256}(3C+40D+70E)^2 + \frac{675}{64}(C+8D-14E)^2 \right. \right. \\ & \left. \left. - \frac{27}{128}(3C+40D+70E)(19C-120D+70E) \right] N^2 + (A+3B) \cdot \Delta \cdot M \right. \\ & \left. + \left[\frac{9}{8}(3C+40D+70E) - \frac{3}{8}(19C-120D+70E) \right] (0.5\Delta) N \right\}^{\frac{1}{2}} \end{aligned}$$

where the (+) combination is the energy of the upper A_1 state derived from $E_g(O_h)$. The energy expression for the A_1 ground state is then subtracted from the expressions for the excited A_1, B_1 and B_2 states. The three resulting expressions are equivalent to the experimentally determined energies for the $A_1 \rightarrow A_1, A_1 \rightarrow B_1$ and $A_1 \rightarrow B_2$ electronic transitions of Fe^{2+} in C_{2v} symmetry. Hence, there are three equations containing three unknowns, Δ , M and N , and the point-charge model can be solved exactly.

REFERENCES

- Ballhausen, C. J. (1962) Introduction to Ligand Field Theory. McGraw Hill, New York.
- Figgis, B. N. (1966) Introduction to Ligand Fields. Interscience Publishers.
- Ghose, S. (1965) $Mg^{2+}-Fe^{2+}$ order in an orthopyroxene, $Mg_{0.93}Fe_{1.07}Si_2O_6$.
Z. Kristallogr. 122, 81-99.
- Goldman, D. S. and G. R. Rossman (1976) The spectra of orthopyroxene revisited: the splitting of the ${}^5T_{2g}$ ground state. Amer. Mineral. 61.
- Hutchings, M. T. (1964) Point-charge calculations of energy levels of magnetic ions in crystalline electric fields. Solid State Phys. 16, 227-273.
- Wilson, E. B., J. C. Decius and P. C. Cross (1955) Molecular Vibrations, McGraw Hill, New York.

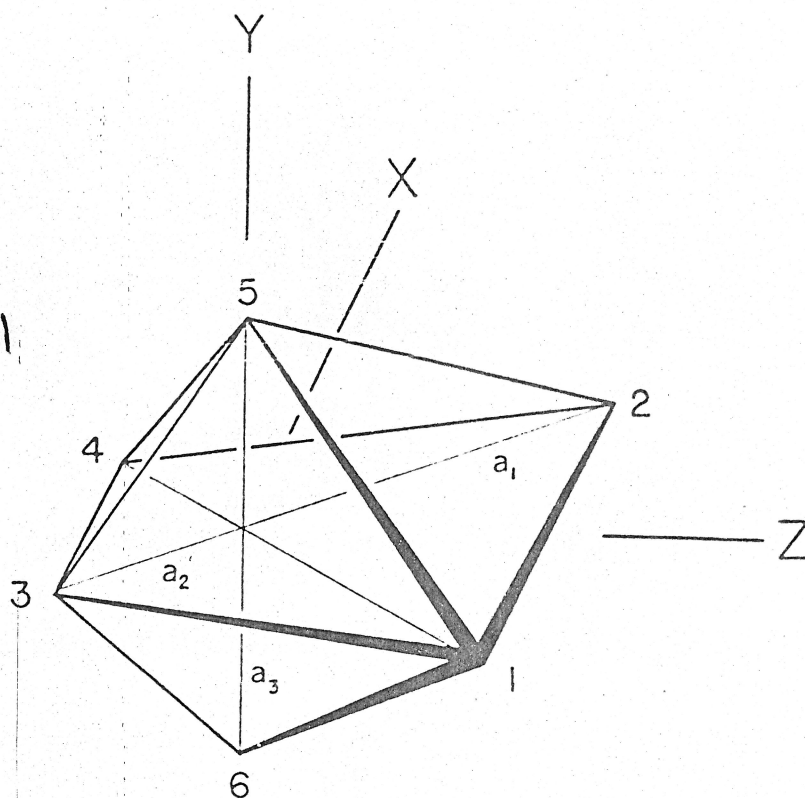


Figure 1. Idealized C_{2v} coordination site in which Z, the two-fold rotation axis, is a dihedral axis. Points 1 through 6 have (r, θ, ϕ) coordinates of (a_1, θ_1, π) , $(a_1, \theta_1, 0)$, (a_2, θ_2, π) , $(a_2, \theta_2, 0)$, $(a_3, \theta_3, \pi/2)$ and $(a_3, \theta_3, 3\pi/2)$, respectively.