

## MINERALOGICAL NOTES

### SELECTION RULES AND ASSIGNMENTS FOR THE SPECTRA OF FERROUS IRON IN PYROXENES

WILLIAM B. WHITE AND KENNETH L. KEESTER, *Materials Research  
Laboratory and Department of Geochemistry and Mineralogy,  
Pennsylvania State University,  
University Park, Pennsylvania.*

#### INTRODUCTION

Bancroft and Burns (1967) on the basis of polarized optical spectra and Mossbauer spectra have arrived at an alternative interpretation of the optical spectra of  $\text{Fe}^{2+}$  in pyroxenes. In a reconnaissance of  $\text{Fe}^{2+}$  spectra in silicates White and Keester (1966) assigned some low frequency bands of pyroxene spectra to traces of tetrahedral ferrous iron on grounds that seemed reasonable from unpolarized spectra. Bancroft and Burns, having polarized spectra, choose an alternative interpretation of assigning these bands to spin-allowed transitions between levels split apart by the highly distorted oxygen polyhedron of the M(2) site in the pyroxene structure.

Their new interpretation may have great consequences because, if correct, the optical spectrum could provide a powerful new tool for structural interpretation. Because of its structural importance we have reexamined the spectra of our pyroxene crystals using polarized radiation and have looked rather carefully at the theoretical implications.

#### EXPERIMENTAL

Single crystal spectra were obtained on a Beckman model DK-2A spectrometer. The crystals were oriented with petrographic and Federov microscopes. The crystals were described in the earlier study (White and Keester, 1966). Polarized spectra were obtained using a pair of matched calcite Glan prisms in both sample and reference beams. These prisms are transparent in the near infrared and give good results to  $2.9 \mu$ .

#### SPECTRA AND SELECTION RULES

A remeasurement of the spectrum of enstatite with polarizers gave results essentially in agreement with Bancroft and Burns. Unfortunately the polarizers did not transmit far enough into the infrared to determine the polarization of the  $3100 \text{ cm}^{-1}$  band.

As Bancroft and Burns correctly state, an ion on a regular or near-regular tetrahedral site would give nearly the same spectrum in all polarization directions. It is therefore concluded that Bancroft and Burns

may have provided a better interpretation for the low-frequency bands than the model suggested by us. It remains to examine the assignments proposed by Bancroft and Burns and to investigate the implications of their model.

This discussion is concerned only with the broad, spin-allowed bands. In  $\text{Fe}^{2+}$  these are the quintet levels derived from the  ${}^5\text{D}$  free ion state. In an octahedral field the  ${}^5\text{D}$  level splits into an upper  $\text{E}_g$  level and a lower  $\text{T}_{2g}$  level. In fields of progressively lower symmetry these levels are further split until all degeneracy is removed and a maximum of five quintet levels are resolved. The difficulty arises when one attempts to assign relative energies and symmetry labels to these states.

The true symmetry of the M(2) site in orthopyroxene is  $C_1$  but the polarization dependence of the spectra indicates that some sort of higher pseudo-symmetry is effective. One way in which the labeling is often done is by a descent of symmetry beginning with the octahedron and progressively lowering the symmetry. The labeling of states can then be determined from tables. This method was used by Bancroft and Burns. Unfortunately Bancroft and Burns used the descent-of-symmetry table from Cotton (1963) which is incomplete. The coordinate axes of published character tables are defined by selecting the highest symmetry axis as the  $z$ -axis. The reduction of  $D_{4h}$  to  $C_{2v}$  symmetry can be done in four different ways depending which symmetry element of  $D_{4h}$  degenerates into the unique two-fold axis of  $C_{2v}$ . In Cotton's table only the case in which the four-fold axis reduces to the two-fold axis is given. A portion of structure, the M(2) coordination polyhedron, of orthopyroxene, adapted from Ghose (1965), is shown in Figure 1. It can be seen that the pseudo two-fold axis,  $C_2$ , of the M(2) site lies parallel to the crystallographic  $b$ -axis and bisects the angle between the two long bonds. It is derived from one of the two-fold axes, not the four-fold axis of  $D_{4h}$  and lies between the bonds, rather than along the bonds as does the axis selected by Bancroft and Burns. The result changes the symmetry labeling of the states and therefore the selection rules. Several possibilities derived from the selection of the pseudo two-fold axis shown in Figure 1 have been determined using the complete descent-of-symmetry tables given by Wilson, Decius, and Cross (1955). These are shown in Figure 2 along with the allowed transitions.

Bancroft and Burns did not indicate how they calculated their selection rules so a very brief outline is given here. Transitions between  $d$ -orbital levels are formally forbidden as dipole transitions by Laporte's Rule. Two mechanisms are primarily responsible for the relaxation of this selection rule. In centrosymmetric coordinations the transitions become weakly allowed by coupling between electronic states and lattice

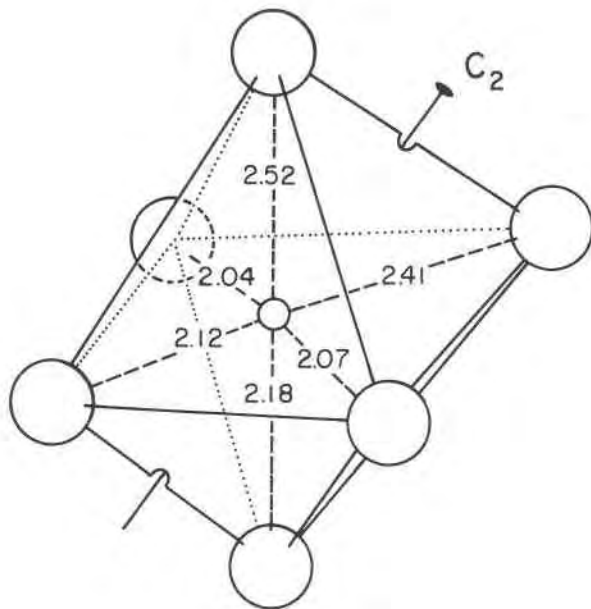


FIG. 1. Structural arrangement of the M(2) site in orthopyroxene showing the placement of the pseudo-two-fold axis, perpendicular to the "original" four-fold axis consisting of two short bonds (modified from Ghose, 1965).

vibrations. In noncentrosymmetric coordinations such as those under discussion here, there may be mixing between the even  $d$ -orbital wave functions and odd wave functions usually from higher lying  $p$ -orbitals. This mixing adds a certain amount of odd character to the  $d$ -orbitals and gives rise to dipole spectra typically 10 to 100 times as intense as the vibrationally coupled spectra. The transition probabilities for such spectra are given by integrals of the type

$$P_{mn} \sim \int \psi_n^* \mu \psi_m d\tau$$

where  $\Psi_m$  and  $\Psi_n$  are the wave functions for the excited and ground states and  $\mu$  is the dipole moment operator. The only way that the transition probability can have a finite value is that the integral be totally symmetric. This can be determined from the symmetry of the energy states by constructing direct products of the irreducible representations of the wave functions with the irreducible representations of the dipole operator (which transforms as  $x$ ,  $y$  or  $z$ ). An elementary account of these calculations is given by Cotton (1963). From the character tables of  $C_{2v}$  all combinations were constructed of direct products for the energy levels of

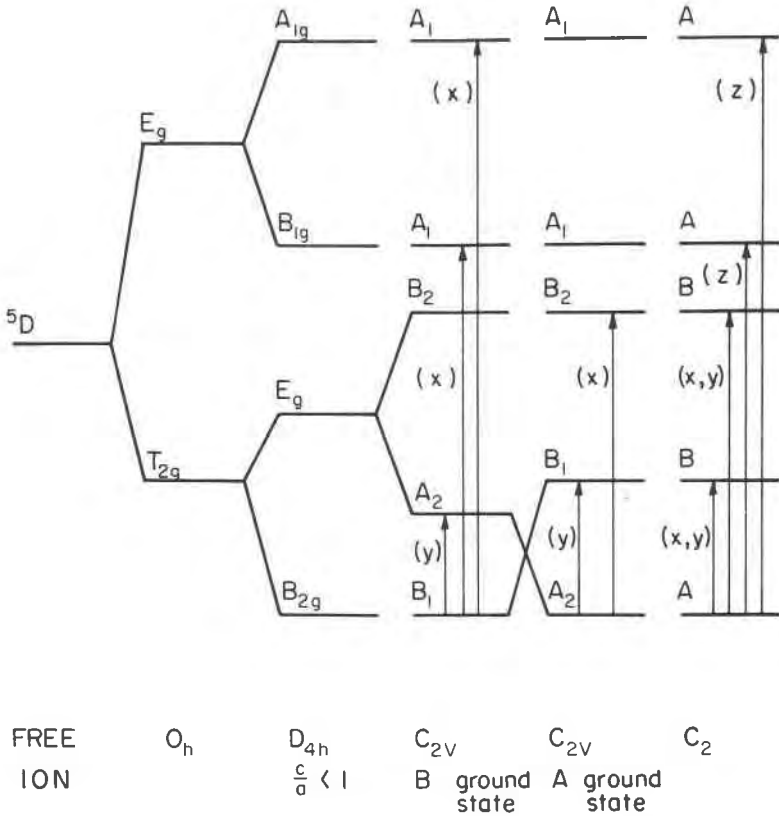


FIG. 2. Energy level schemes for  $Fe^{2+}$  on the M(2) site of orthopyroxene assuming various site symmetries and ground states  $B_1$  and  $A_2$ .

Figure 2 with the three components of the dipole operator. Since all levels are nondegenerate, the representations and direct products are all one-dimensional. Those combinations whose direct product transformed as  $A_1$  are formally allowed and these are shown by the arrows in Figure 2. In parenthesis are shown the components of the dipole moment that couple the transitions.

The polarization behavior of the spectra is obtained by relating the electronic symmetry axes of the coordination polyhedron to the crystallographic axes and vibration directions of orthopyroxene. The  $z$ -axis is the pseudo-two-fold axis which is parallel to the  $b$ -crystallographic axis and the  $\alpha$  polarization direction so

$$z = b = \alpha$$

The  $x$  and  $y$  symmetry axes are not well defined except that they lie in the  $ac$  plane.

$$x = (a, c) = (\beta, \gamma)$$

$$y = (a, c) = (\beta, \gamma)$$

The results obtained here differ rather markedly from those of Bancroft and Burns. Their energy level scheme with one transition appearing in each vibration direction depends on assigning an  $A_1$  ground state. With the symmetry reduction given above the  $A_1$  levels are obtained from the splitting of the  $E_g$  excited state. The accidentally good agreement they obtained between their spectrum and their energy level diagram was achieved by an unreasonable placement of the major symmetry axis. However, there is no agreement between the predicted transitions of Figure 2 and the observed spectrum. In particular, no bands are permitted with polarization parallel to  $\alpha$  which is in reality the strongest band in the spectrum.

There are two escapes from the dilemma. One is to assume that the M(2) site is so distorted that the descent of symmetry argument is invalid and that the  $A_1$  level is lowered sufficiently to become the ground state. The other is to lower the pseudosymmetry still further to  $C_2$ . The latter explanation appears to be the more reasonable. The energy levels and selection rules for a  $C_2$  site symmetry with an  $A$  ground state are also shown in Figure 2.

In the energy level scheme derived by Bancroft and Burns one of the four possible transitions is forbidden by the selection rules. In the scheme assuming  $C_2$  point symmetry all transitions are allowed; two are polarized parallel to the  $z$ -axis and two perpendicular to the  $z$ -axis. Thus one more spectral band is predicted for the orthopyroxene structure. Even if Bancroft and Burns' energy level labeling were correct, deviations from the pseudosymmetry and vibronic coupling should make this band at least weakly allowed and it should have been observed in thick crystals. Since it was not observed in the spectral range examined, there are three possibilities: (1) it may be exactly coincident or overlapped with one of the observed bands due to one energy level moving down while another moves up, (2) it may lie below the range of measurement and be obscured by the lattice vibrations in the infrared, or (3) it may be above the previous level of measurement in the ultraviolet where it would be obscured by or incorporated into other strong "charge transfer" bands. Calculations based on Mössbauer spectra by Marzolf, Dehn, and Salmon (in press) suggest that the missing level occurs near 750–800  $\text{cm}^{-1}$ .

## APPLICATION TO OTHER DISTORTED SITES

The very large splittings generated by the distorted pyroxene site are most interesting. Many spectra of transition metals in distorted sites have been published and in general such effects of the site distortion do not seem to have been observed. Holmes and McClure (1957) found only a single band in the spectrum of chalcantite,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in spite of a rather determined effort to separate the expected bands by a gaussian fitting of the band contours. Likewise in diopside, in which copper is in an approximately square planar configuration, only one band was observed in the range of 20,000 to 3500  $\text{cm}^{-1}$  (Newnham and Santoro, 1967). The blue color of kyanite has been determined (White, and White, submitted) to be due to  $\text{Ti}^{3+}$  in a distorted site in the triclinic structure yet only one band is observed. H. Kasper (in press) reports that the spectra of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in the pseudo-brookite structure show very little extra splitting.

The situation observed in the iron-containing silicates may allow for the first time an estimate of the degree of site distortion necessary to produce an observable splitting in the spectrum. The coordination polyhedron of actinolite is a nearly regular octahedron with the metal-oxygen distance,  $R = 2.11 \text{ \AA}$ . (Zussman, 1955) and only a slight splitting occurs. Olivine (Hanke and Zemann, 1963) has a range of  $R$  on the pseudotetragonal site of 2.08 to 2.14  $\text{ \AA}$  and a range of  $R$  on the pseudotrigonal site of 2.06  $\text{ \AA}$  to 2.17  $\text{ \AA}$ . The maximum splitting of the excited state (*e.g.* orbital) is about 3000  $\text{cm}^{-1}$ . A newly observed band in the infrared spectrum at 1670  $\text{cm}^{-1}$  which may be due to  $\text{Fe}^{2+}$  puts an upper limit of that amount on the ground state ( $t_{2g}$  orbital) splitting. The new feature which appears in the pseudomonoclinic M(2) site in the pyroxene structure is that the bonds on opposite sites of the metal atom are not the same length (Fig. 1). In diopside (Morimoto, Appleman and Evans, 1960) these range from 2.06 to 2.16  $\text{ \AA}$ . The excited state is split by roughly 4000  $\text{cm}^{-1}$  and the ground state by 4500  $\text{cm}^{-1}$ . The more distorted of the two cation sites in hypersthene (Ghose, 1965) has bond lengths ranging from 2.04 to 2.52  $\text{ \AA}$ . The excited state levels are so highly split that one level is completely lost and the ground state is split by 5500  $\text{cm}^{-1}$ .

## CONCLUDING COMMENTS

The object of this short discussion has been to underline the implications of Bancroft and Burns' new interpretation of the pyroxene spectra, to suggest a modification of their assignments and to provide some new data indicating that the situation is still more complicated. While this

new interpretation seems to be more correct, it is not conclusive. Other work now in progress (Burns, 1966; Lewis and White, 1967) promises to shed more light on the situation.

## ACKNOWLEDGEMENTS

The problems of the pyroxene spectra were discussed with a number of people and we are particularly grateful to Professor R. E. Newnham, Dr. James Dehn and Dr. Horst Kasper for their opinions. We are particularly grateful to Dr. Roger Burns for an opportunity to discuss his interpretation in advance of publication. This research is supported by the National Science Foundation under Grant No. GP 3232.

## REFERENCES

- BANCROFT, G. M., AND R. G. BURNS. (1967) Interpretation of the electronic spectra of iron in pyroxenes. *Amer. Mineral.* **52**, 1278-1287.
- BURNS, R. G. (1966) Electronic spectra, crystal field phenomena, and iron-magnesium ratios in coexisting pyroxenes and amphiboles (Abstr.) *Int. Mineralog. Ass. Cong.*, Cambridge.
- COTTON, F. A. (1963) *Chemical Applications of Group Theory*, Interscience Publishers, New York.
- 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.
- HANKE, K. AND J. ZEMANN (1963) Verfeinerung der Kristallstruktur von Olivin. *Naturwissenschaften* **50**, 91.
- HOLMES, O. G., AND D. S. McCLURE (1957) Optical spectra of hydrated ions of the transition metals. *J. Chem. Phys.* **26**, 1686-1694.
- LEWIS, J. F. AND W. B. WHITE (1967) Correlations of optical spectra with structural environment of  $Fe^{++}$  in pyroxenes. *Trans. Amer. Geophys. Union* **48**, 233.
- MORIMOTO, N., D. E. APPLEMAN, AND H. T. EVANS, JR. (1960) The crystal structures of clinoenstatite and pigeonite. *Z. Kristallogr.* **114**, 120-147.
- NEWNHAM, R. E. AND R. P. SANTORO (1967) Magnetic and optical properties of diopside. *Phys. Status Solidi* **19**, K87-K90.
- WHITE, W. B. AND K. L. KEESTER (1966) Optical absorption spectra of iron in the rock-forming silicates. *Amer. Mineral.* **51**, 774-791.
- WHITE, E. W. AND W. B. WHITE. Electron probe and optical absorption study of kyanite. *Science* (in press).
- WILSON, E. B., JR. J. C. DECIUS, AND P. C. CROSS (1955). *Molecular Vibrations*. McGraw-Hill, New York.
- ZUSSMAN, J. (1955) The crystal structure of an actinolite. *Acta Crystallogr.* **8**, 301-308.