

INTERPRETATION OF THE ELECTRONIC SPECTRA OF IRON IN PYROXENES

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ABSTRACT

Measurements of polarized absorption spectra of orthopyroxenes and a staurolite together with Mössbauer measurements of orthopyroxenes, show that the earlier interpretation (White and Keester, 1966) of the unpolarized spectra of pyroxenes is incomplete. An alternative explanation of the pyroxene spectra, taking into account the additional information obtained from polarized spectra and Mössbauer measurements, is presented and new band assignments made. The present study does not support the suggestion made by White and Keester that Fe^{2+} ions occur in tetrahedral coordination substituting for silicon in the SiO_4 tetrahedra of pyroxenes. This paper shows that some of the spectral characteristics of Fe^{2+} in tetrahedral coordination can also be shown by Fe^{2+} in a very distorted octahedral environment, such as those in many silicate structures. Cation ordering and coordination site symmetry in the orthopyroxene structure are discussed.

INTRODUCTION

In a recent study of unpolarized absorption spectra of rockforming silicates (White and Keester, 1966), it was suggested that small amounts of Fe^{2+} ions occur in tetrahedral coordination substituting for silicon in the structures of pyroxenes. Three reasons were given in support of this suggestion. The first was a correlation of the positions and intensities of the absorption bands of diopside (4420 cm^{-1}) and enstatite (5430 cm^{-1}) with bands of Fe^{2+} -doped ZnO (4500 cm^{-1}) and MgAl_2O_4 (4300 cm^{-1}) where ions are known to occur in tetrahedral coordination. The second reason was the mathematical relationship that exists between tetrahedral and octahedral crystal-field splittings in transition-metal ions. The third reason was a correlation of the iron position in the riebeckite structure with that of the pyroxene structure.

In the present paper, the authors wish to present an alternative interpretation of the pyroxene spectra based on polarized electronic spectra and Mössbauer measurements of orthopyroxenes and a staurolite.

In previous studies of crystal-field spectra of iron-containing minerals (Farrell and Newnham, 1965; White and Keester, 1966) it has been as-

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sumed, to simplify interpretations of the spectra, that Fe^{2+} ions occur in coordination sites which approximate closely octahedral and tetrahedral symmetry. In weak octahedral crystal-fields, only one spin-allowed transition is permitted for the Fe^{2+} ion, ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$, which is allowed through a vibronic coupling mechanism (Cotton, 1963, p. 231). In tetrahedral fields, one spin-allowed transition is again permitted for the Fe^{2+} ion, ${}^5\text{E} \rightarrow {}^5\text{T}_2$, which is allowed by simple changes in the electronic wavefunctions (Cotton, 1963, p. 237). Such transitions should lead to one band in an absorption spectrum of an iron (II) compound, which may be broadened by the Jahn-Teller effect (Cotton and Myers, 1960). In general, tetrahedral Fe^{2+} should give rise to absorption bands 10 to 100 times more intense than those due to Fe^{2+} in centrosymmetric, octahedral coordination (Cotton, 1963, p. 238).

However, coordination sites in crystal structures of ferromagnesian silicates rarely have octahedral or tetrahedral symmetry. Oxygen coordination polyhedra are invariably distorted, and often strong next-nearest neighbor interactions exist (Burns, 1965; 1966 a). These effects lower from cubic the symmetry of crystal-fields within such coordination sites. Three consequences are: first, the degeneracies of the ${}^5\text{T}_{2g}$ and ${}^5\text{E}_g$ states of the Fe^{2+} ion in an octahedral crystal-field, and the ${}^5\text{E}$ and ${}^5\text{T}_2$ states in a tetrahedral field, are removed making possible additional spin-allowed transitions; second, the intensities of absorption bands in low-symmetry crystal-fields are often polarization dependent, which is not the case in octahedral and tetrahedral crystal-fields; and third, absorption bands may be greatly intensified if the coordination polyhedron is noncentrosymmetric, because the transitions are allowed not only by vibronic coupling but also by simple changes in the electronic wave functions.

EXPERIMENT AND RESULTS

Electronic Spectra. Polarized spectral measurements over the range 4000–25000 Å were made by a microscope technique (Burns, 1966b). The polarized spectra of an orthopyroxene with 14.5 percent FeSiO_3 are shown in Figure 1a. Each spectrum is distinctive: the α spectrum consists of a very intense band at 10970 cm^{-1} ; the β spectrum contains two intense bands of comparable intensity at 5380 cm^{-1} and 11150 cm^{-1} , respectively; and the γ spectrum consists of a weak bands at 5380 cm^{-1} and 11140 cm^{-1} . The positions of the absorption bands are comparable with those measured by White and Keester (1966) at 5430 cm^{-1} and 11000 cm^{-1} in the unpolarized spectrum of an orthopyroxene with about 12 percent FeSiO_3 . However, in the polarized spectra (Fig. 1a), the absorption band at 5380 cm^{-1} is most intense in the β spectrum, occurs

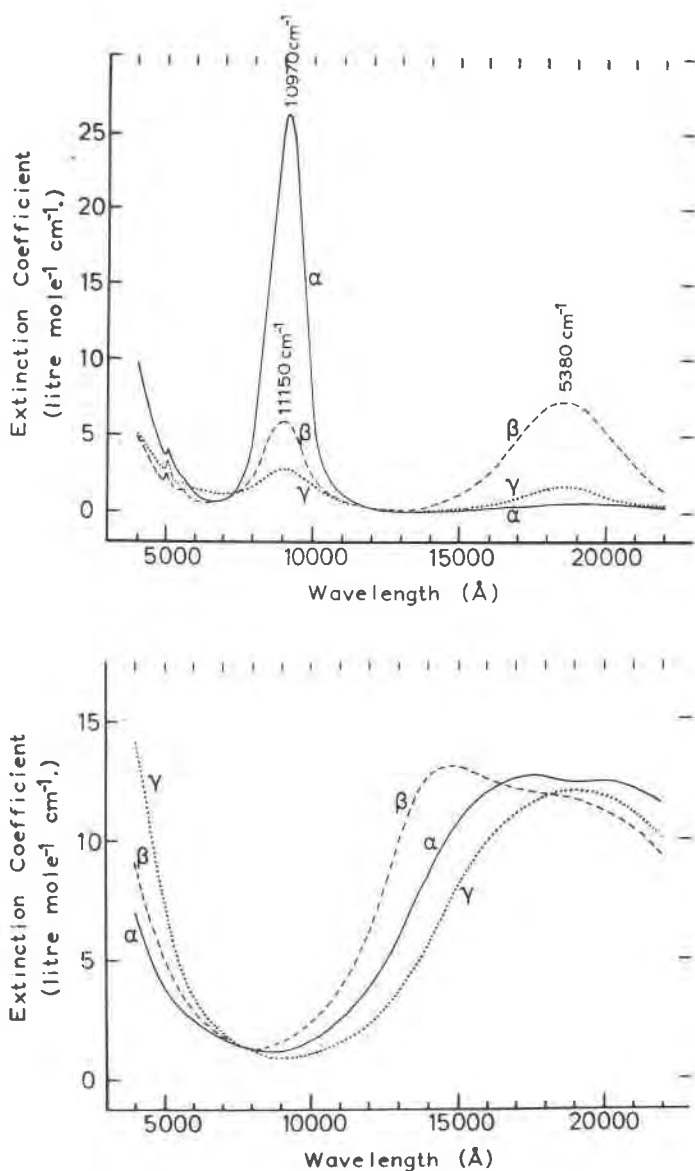


FIG. 1. Polarized absorption spectra of an orthopyroxene and a staurolite: (a, above) spectra of a bronzite with 14.5% FeSiO₃. The specimen is from Bamle, Norway. ($\alpha=b$; $\beta=a$; $\gamma=c$); (b, below) spectra of a staurolite with 12.22 wt. % FeO. The specimen is from Pizzo Forno, Switzerland. ($\alpha=b$; $\beta=a$; $\gamma=c$).

weakly in the γ spectrum and is almost absent in the α spectrum. Similar features have been found in the polarized spectra of other orthopyroxenes with compositions ranging from 8.1 to 86.4 percent FeSiO_3 (Burns, to be published), although absorption maxima of all bands shift to longer wavelengths with increasing iron concentration. In particular, the intensities of the bands in the regions $5400\text{--}4900\text{ cm}^{-1}$ and $11200\text{--}10750\text{ cm}^{-1}$ in the β spectra are comparable throughout the orthopyroxene series. The band assignments and interpretation of the orthopyroxene spectra will be discussed in detail in a later paper.

The polarized spectra of a staurolite containing 12.22 weight percent FeO , in which Fe^{2+} ions are known to occur in tetrahedral coordination, are shown in Figure 1b. for reference. Each spectrum contains a broad, intense band spanning the region $14000\text{--}22000\text{ \AA}$. The intensities of the bands in all three polarized spectra are comparable and lower than that of the band at 10970 cm^{-1} in the orthopyroxene α spectrum (Fig. 1b).

Mössbauer spectra. The Mössbauer instrumentation and technique are described elsewhere (Bancroft, Maddock and Ward, 1965; Bancroft, Burns and Maddock, 1967). Measurements have been made on seven orthopyroxenes with compositions ranging from 14.5 to 86.4 percent FeSiO_3 (Bancroft and Burns, 1967 a, b). The spectra of the orthopyroxene $\text{Fs}_{14.5}$ consists of a simple doublet which, at room temperature, has a chemical isomer shift of 1.25 mm/sec relative to a stainless steel source and a quadrupole splitting of 2.11 mm/sec. These values are in agreement with those measured by other workers (de Coster, Pollak and Amelinckx, 1963; Sprengel-Segel and Hanna, 1964). At the temperature of liquid nitrogen, the quadrupole splitting increases to 2.16 mm/sec. In the Mössbauer spectra of orthopyroxenes exceeding about 35 percent FeSiO_3 , a second quadrupole doublet appears which has values for the chemical isomer shift and quadrupole splitting of 1.25–1.28 mm/sec and 2.35–2.46 mm/sec, respectively.

INTERPRETATION OF THE SPECTRA

The orthopyroxene structure contains two positions of six-fold coordination (Byström, 1943; Ghose, 1965; Burnham, 1966). The coordination polyhedron about the $M(1)$ position is approximately octahedral, but the $M(2)$ coordination site is strongly distorted from octahedral symmetry. The Mössbauer measurements show that Fe^{2+} ions enter the $M(2)$ position preferentially in the orthopyroxene structure, and that in the bronzite, $\text{Fs}_{14.5}$, less than ten percent of the total iron is present in the $M(1)$ position (Bancroft, Burns and Howie 1967). This result is in ac-

cord with X-ray diffraction measurements of a granulite facies hypersthene, $\text{Fs}_{53.3}$, which showed that iron occurs predominantly in the $M(2)$ position (Ghose, 1965; Burnham, personal communication).

The observed spectra (Fig. 1a) may be interpreted as transitions within the Fe^{2+} ion in the $M(2)$ position of the orthopyroxene structure. The point symmetry of this position is C_1 , but for the purposes of the present discussion, the molecular symmetry of the $M(2)$ coordination polyhedron may be approximated to C_{2v} . In a crystal-field of symmetry

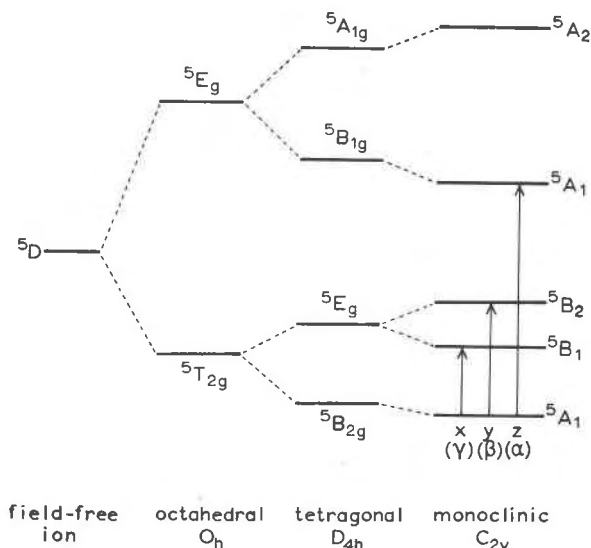


FIG. 2. Energy level diagram for the Fe^{2+} ion in crystal-fields of different symmetries: (a.) octahedral, O_h (b.) tetragonal, D_{4h} , with compression along the tetrad axis. (c.) monoclinic, C_{2v} . Allowed transitions are shown.

C_{2v} , the octahedral ${}^5T_{2g}$ ground-state for the Fe^{2+} ion is resolved into the lower 5A_1 , 5B_1 , and 5B_2 states, and the 5E_g excited state into the upper 5A_1 and 5A_2 states (Fig. 2). Either the 5A_1 , 5B_1 or 5B_2 states may be the ground-state for the Fe^{2+} ion in a symmetry C_{2v} crystal-field. In order to account for the polarization dependence of the absorption band at 5380 cm^{-1} in the orthopyroxene β spectrum, transitions between only the three lower states 5A_1 , 5B_1 and 5B_2 need to be considered. Taking each state in turn as the ground-state, two spin-allowed transitions are possible to the other lower states, which leads to a total of six different transitions by variation of the ground-state. In addition, each transition may take place for the three polarizations of the electric vector with respect

to the electronic axes x , y and z . Therefore, 18 transitions are possible between the lower states 5A_1 , 5B_1 and 5B_2 using polarized radiation. Selection rules, however, show that only four of these transitions are allowed by the symmetry of the electronic wave function (Cotton, 1963, appendix II). They are:

$${}^5A_1 \rightarrow {}^5B_1, \quad \text{allowed parallel to } x;$$

$${}^5A_1 \rightarrow {}^5B_2, \quad \text{allowed parallel to } y;$$

$${}^5B_1 \rightarrow {}^5A_1, \quad \text{allowed parallel to } x;$$

and

$${}^5B_2 \rightarrow {}^5A_1, \quad \text{allowed parallel to } y.$$

Therefore, no matter what the ground-state may be in a symmetry C_{2v} crystal-field, a transition between the lower states is allowed in one electronic direction only, which should produce an absorption band at a particular frequency in one polarized spectrum only. However, vibronic coupling and the noncoincidence of the electronic axes x , y and z with the polarization axes α , β and γ may result in a small component of the allowed transition producing weak absorption in the other polarized spectra. Thus, the intense band in the β spectrum and weak band in the γ spectrum at 5380 cm^{-1} in the orthopyroxene spectra represent a transition between the states derived from the octahedral ${}^5T_{2g}$ state. It is tempting to designate 5A_1 as the ground-state of the Fe^{2+} ion in the $M(2)$ position of the orthopyroxene structure, and to assign the two bands at 5430 cm^{-1} and 3100 cm^{-1} in the unpolarized spectra (White and Keester, 1966) to transitions to the 5B_1 and 5B_2 states. The absorption band at 11000 cm^{-1} could represent the transition ${}^5A_1 \rightarrow {}^5A_1$. The transition ${}^5A_1 \rightarrow {}^5A_2$ is not allowed in a symmetry C_{2v} crystal-field, and is not observed in the polarized spectra of the orthopyroxene with 14.5 percent FeSiO_3 .

The staurolite structure contains Fe^{2+} ions in tetrahedral coordination (Náray-Szabó and Sasvári, 1958). The FeO_4 tetrahedron is slightly distorted from tetrahedral symmetry, but the distortion is similar to that of the SiO_4 tetrahedra in the orthopyroxene structure (Ghose, 1965). The spectra of staurolite (Fig. 1b) represent transitions in the Fe^{2+} ion between components of the 5E ground-state and 5T_2 excited state. These transitions lead to the broad absorption bands in all three polarized spectra spanning the region $14000\text{--}22000 \text{ \AA}$.

DISCUSSION

The interpretation of the orthopyroxene spectra shows that the absorption band at 5380 cm^{-1} is due to a transition within Fe^{2+} ions

situated in a six-fold coordination site of the orthopyroxene structure. This assignment differs from that given by White and Keester (1966), who believe that the band at 5430 cm^{-1} in the enstatite spectrum arises from Fe^{2+} ions in tetrahedral coordination in the orthopyroxene structure. An absorption band at 4420 cm^{-1} in diopside was also attributed by White and Keester to Fe^{2+} ions in tetrahedral coordination. The crystal structure of diopside (Warren and Bragg, 1929) shows that the six-fold coordination site is distorted from octahedral, although the distortion is not as large as that of the orthopyroxene $M(2)$ site. The band at 4420 cm^{-1} in diopside may also be assigned to a transition between resolved components of the ${}^5T_{2g}$ ground-state of the Fe^{2+} ion in six-fold coordination.

The energy separations 5430 cm^{-1} (enstatite) and 4420 cm^{-1} (diopside) between the lower states of the Fe^{2+} ion in the pyroxene structure are not unreasonable when a comparison is made with square planar Fe^{2+} in gillespite. The spectra of gillespite (Burns, Clark and Stone 1966) show that the octahedral ${}^5T_{2g}$ state is resolved into 5E_g and ${}^5B_{2g}$ states separated by about 6500 cm^{-1} in a symmetry D_{4h} crystal-field. In addition, the quadrupole splitting and the temperature dependence of the quadrupole splitting in the Mössbauer spectra of orthopyroxene are consistent with the large separations between the lower states derived from ${}^5T_{2g}$ for the Fe^{2+} ion in a distorted octahedral site (Ingalls, 1964; Clark, Bancroft and Stone, 1967).

White and Keester (1966) correlated absorption bands in diopside and enstatite with bands arising from Fe^{2+} ions in the ZnO and spinel structures, in which Fe^{2+} is in tetrahedral coordination. This correlation may be negated by the staurolite spectra (Fig. 1b). It was noted earlier that the FeO_4 polyhedron in staurolite is similar to the SiO_4 tetrahedron in the orthopyroxene structure. If Fe^{2+} ions were in tetrahedral coordination in pyroxenes, absorption bands with comparable intensity should be observed in all three polarized spectra by analogy with the staurolite spectra. The band at 5380 cm^{-1} in the orthopyroxene spectra, however, is polarization dependent: it is most intense in the β spectrum and is virtually absent in the α spectrum.

White and Keester (1966) note that peaks caused by iron in tetrahedral coordination are of much greater intensity (10 to 100 times) than those arising from iron in octahedral coordination. They conclude that only small amounts of iron (of the order of 0.1 percent) in tetrahedral coordination would be necessary to account for the intensity of the peak at 5430 cm^{-1} in enstatite compared with the peak at 11000 cm^{-1} originating from octahedral iron. The intensity ratio 10–100:1 for tetrahedral:octahedral ion transitions applies only if the octahedral environment is centrosymmetric. This is not the case for the orthopyroxene $M(2)$ coor-

dination site. In fact, the intensity of the band at 10970 cm^{-1} in the orthopyroxene α spectrum is higher than those of the bands in the staurolite spectra which originate from tetrahedral iron. Even in the orthopyroxene β spectrum the intensity of the band at 11150 cm^{-1} is more than three times more intense than those for centrosymmetric Fe^{2+} complexes (Cotton and Meyers, 1960). High intensities are also found in the polarized spectra of other ferromagnesian silicates (Burns 1967). An absorption band at 10780 \AA in the γ spectrum of fayalite, for example, has a molar extinction coefficient of about $8\text{ l. mole}^{-1}\text{ cm}^{-1}$, and originates from Fe^{2+} ions in the noncentrosymmetric, six-coordinate $M(2)$ site of the olivine structure. Therefore, the evidence for tetrahedral Fe^{2+} in pyroxenes based on peak intensities is unfounded. Furthermore, it would be fortuitous if the ratio of Fe^{2+} ions in tetrahedral coordination remained constant throughout the orthopyroxene series, which would be necessary to explain the equal intensities of the two bands at $5400\text{--}4900\text{ cm}^{-1}$ and $11200\text{--}10750\text{ cm}^{-1}$ in the orthopyroxene β spectrum.

Other evidence cited by White and Keester (1966) for tetrahedral Fe^{2+} in pyroxenes included the relationship between the octahedral and tetrahedral crystal-field splitting parameters, Δ_0 and Δ_t respectively. The relationship $\Delta_t = 4/9\Delta_0$, which is derived from the point-charge model of crystal-field theory, requires that the metal, anions, and metal-anion distances be identical in the two coordinations. In addition, the crystal-field parameter, Δ , is proportional to the inverse fifth power of the interatomic distance (Dunn, McClure and Pearson, 1965, p. 81), which means that a small contraction of metal-oxygen distances produces a large change in Δ . White and Keester (1966) noted that the band at 4420 cm^{-1} in the diopside spectrum is located at an energy almost $4/9$ that of the 9730 cm^{-1} band attributed to iron in octahedral coordination. They also noted that the band at 5430 cm^{-1} in the enstatite spectrum occurs at an energy 25 percent higher than that attributed to tetrahedral Fe^{2+} in diopside. In the diopside structure, the average silicon-oxygen distance is 1.61 \AA , whereas the average distance is 2.10 cm^{-1} in the six-fold coordination site (Warren and Bragg, 1929). Similarly, the orthopyroxene structure (Ghose, 1965) has mean distances $\text{Si}-\text{O} = 1.628\text{ \AA}$, $M(2)-\text{O} = 2.220\text{ \AA}$ and $M(1)-\text{O} = 2.092\text{ \AA}$. Therefore, the silicon-oxygen distances are comparable in the two pyroxene structures. If iron were to replace silicon in both diopside and enstatite, the absorption bands arising from tetrahedral Fe^{2+} should occur at similar energies and not differ by 25 percent. Furthermore, replacement of silicon by iron in diopside would lead to a large contraction of the metal-oxygen distances compared with six-fold coordinated iron. This would result in Δ_t being considerably larger than the value expected for iron in a tetrahedral site with metal-oxygen distances of about 2.10 \AA . Therefore, the

absorption bands at 4420 cm^{-1} and 9730 cm^{-1} in the diopside spectrum cannot be explained by the occurrence of iron in both octahedral and tetrahedral coordination. A similar argument applies to the bands at 5430 cm^{-1} and 11000 cm^{-1} in the spectrum of enstatite.

Finally, a recent refinement of the crystal structure of riebeckite, $\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{22}(\text{OH})_2$, was cited as evidence by White and Keester (1966) for tetrahedral Fe^{2+} in silicates. In the riebeckite structure, the average silicon-oxygen distance was considered by Colville and Gibbs (1964) to be significantly larger than that expected for amphibole, which suggested that small amounts of iron replaced silicon in tetrahedral coordination. Colville and Gibbs, however, did not designate the oxidation state of iron which substituted for silicon. Substitution of silicon by Fe^{3+} in silicates is well established, and since X-ray diffraction measurements cannot usually differentiate between Fe^{2+} and Fe^{3+} , the occurrence of the smaller Fe^{3+} ion in tetrahedral coordination in riebeckite rather than the larger Fe^{2+} ion, appears to be more plausible. In this connection, it may be noted that no spectral evidence was obtained by White and Keester for tetrahedral Fe^{2+} in actinolite, although Fe^{2+} ions were postulated to occur in tetrahedral coordination in diopside. This difference between actinolite and diopside would have been inconsistent with the observation that Al, and perhaps Fe^{3+} , replaces silicon with equal facility in hornblende and augite, implying that Fe^{2+} should behave similarly.

Substitution of Fe^{2+} ions (radius 0.76 \AA) for Si^{4+} (0.41 \AA) in silicates would not conform with a "rule of thumb" principle of crystal chemistry: that, for two elements to enter into solid-solution in a crystal structure, the sizes of the ions must be comparable or differ by no more than about 15 percent.

CONCLUSION

Measurements of Mössbauer and polarized absorption spectra of orthopyroxenes and a staurolite have been used to provide an alternative suggestion to the proposal that Fe^{2+} ions occur in tetrahedral coordination in pyroxenes. The reasons given by White and Keester (1966) to explain Fe^{2+} ions in tetrahedral sites have been repudiated, and the possibility that Fe^{2+} ions substitute for silicon in SiO_4 tetrahedra has not been proved. The present paper illustrates the usefulness of polarized absorption spectra and Mössbauer measurements for providing information on coordination site symmetry and distortion, and order-disorder phenomena in ferromagnesian silicates.

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