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THE POLARIZED OPTICAL ABSORPTION SPECTRA OF TOURMALINE, CORDIERITE, CHLORITOID AND VIVIANITE: FERROUS-FERRIC ELECTRONIC INTERACTION AS A SOURCE OF PLEOCHROISM[1]

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ABSTRACT

The polarized optical absorption spectra of tourmaline (blue-green), cordierite, chloritoid and vivianite have been measured in the 7,000–30,000 cm^{-1} (1430–330 nm) region.

In the near-infrared region each spectrum exhibits a *d-d* band system assignable to the $^5T_2 \rightarrow {}^5E$ transition of Fe^{2+} in pseudo-octahedral sites. This system is split into two components by the dynamic Jahn-Teller mechanism in the spectra of vivianite and chloritoid.

All spectra show a number of minor features in the visible region that are probably due to spin-forbidden transitions of octahedrally-bonded Fe^{2+}.

The marked visible pleochroism of cordierite, vivianite and to a lesser extent of the tourmalines, is due to a strongly pleochroic band that is considered to be due to the electronic interaction of adjacent Fe^{2+} and Fe^{3+} ions so located in the crystal lattice that certain of their *d*-orbital lobes overlap, in many cases, along specific crystallographic directions. It is suggested that the $Fe^{2+} \rightarrow Fe^{3+}$ interaction is among the more important and widespread causes of pleochroism in ferromagnesian silicates.

INTRODUCTION

The pleochroism of various ferromagnesian silicates (*e.g.*, orthopyroxene) has been considered by Burns (1966) to be due, at least in part, to polarized absorption bands in the ultraviolet region of the spectrum that represent $Fe^{2+} \rightarrow M^{>2+}$ electron transfer processes (where $M^{>2+}$ represents cations such as Al^{3+}, Fe^{3+}, Ti^{3+}, Ti^{4+} etc.). Such pleochroism is manifested by the differing degree to which the low-energy limb of ultraviolet-centered absorption band(s) penetrates the visible region of the spectrum as the orientation of the mineral is changed in polarized light.

According to Burns (1965), visible pleochroism in ferromagnesian silicates is also caused by the polarized "*d-d*" bands which arise from Fe^{2+} in distorted six-corodinate sites. Recently Newnham and Farrell (1967) explained the pleochroism of cordierite on such a basis.

In a recent study of the polarized absorption spectra of certain sheet silicates exhibiting normal pleochroism (Faye, 1968), evidence was found for the $Fe^{2+} \rightarrow (Al^{3+}, Ti^{3+}, Ti^{4+})$ type of interaction such as that proposed by Burns. However, the pleochroism of transverse ($\perp$001) sections of chlorite and biotite, for example, was also found to be markedly influenced by a polarized absorption band centered at 14,000 cm^{-1}($\sim$700 nm). It was proposed that this band is due to the electronic interaction

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(*i.e.*, electron transfer) between Fe^{2+} and Fe^{3+} ions lying in the infinite planes of octahedrally coordinated cations in the sheet silicates. Such an explanation necessarily involves the concept of overlapping *d*-orbitals of adjacent ions as the path for electron transfer.

In this laboratory recent studies of the polarized absorption spectra of a number of iron-bearing minerals (mostly silicates) suggest that the electronic interaction of Fe^{2+} and Fe^{3+} might be among the more important and widespread causes of pleochroism. A principal purpose of this paper is to substantiate this thesis by a detailed consideration of the crystal structures and polarized spectra of selected specimens of tourmaline, cordierite, chloritoid and vivianite.

This work also presents an interpretation of the non-polarized features of the spectra of each of the four minerals and shows how most of these can be assigned to either spin-allowed or spin-forbidden transitions of Fe^{2+} in approximately octahedral sites.

EXPERIMENTAL

Mineral samples.

The specimens of cordierite, vivianite, chloritoid and tourmaline *T-Bl-1* were obtained from Mr. H. R. Steacy, curator of the reference series of the National Mineral Collection, Geological Survey of Canada. Tourmaline *T-Gr-1* was obtained from Mr. L. Moyd, curator of the display series of the National Mineral Collection, National Museum of Canada. The locality of occurrence and partial analyses of these specimens are given in Table 1.

The tourmaline and cordierite specimens were analyzed for Fe^{2+} by a modification of the method of Groves (1951). The remaining analytical data were obtained by methods similar to those previously outlined by Faye (1968, 1968a).

Apparatus and experimental technique.

The relatively large single crystals of the tourmalines, being uniaxial, were simply cut parallel or perpendicular to the *c*-axis with a wire saw. The resulting sections were ground to a thickness suitable for the measurement of the desired spectra.

In preparing vivianite for spectral measurements, sheets of suitable thickness were cleaved from large single crystals, which permitted measurements to be made parallel to the two principal optical directions lying in the basal plane. For measurements along the third principal optical direction, sections perpendicular to the basal plane were obtained by embedding the crystals in a mounting resin, and cutting sections normal to the cleavage plane with a wire saw. The sections were then mounted on glass slides and ground to a thickness suitable for optical measurements.

Sections of chloritoid parallel to (010), which corresponds to the optic plane, were obtained by first identifying the optic plane in a thick cleavage fragment by means of its optical interference figure, embedding the fragment in resin, and then cutting a section parallel to the optic plane, and reducing the section to a suitable thickness. This section

TABLE 1. CHEMICAL ANALYSES, COLOR AND LOCALITY OF MINERALS

Mineral	Density[a]	Locality	Color	Fe^{2+}		Fe^{3+}		Mn		Ti	
				%	[M][b]	%	[M]	%	[M]	%	[M]
Tourmaline T-Bl-1	3.1	Madagascar	Dark Blue	5.2	[2.9]	0.7	[0.4]	0.3	[0.2]	0.25	[0.2]
Tourmaline T-Gr-1	3.1	Unknown	Medium Green	3.5	[1.9]	0.4	[0.2]	0.8	[0.5]	0.25	[0.2]
Cordierite	2.59 (measured)	Madagascar	Blue-Violet	1.4	[0.7]	0.4	[0.2]	0.04	[0.02]		
Chloritoid	3.7	Urals	Dark Green to Black	16.0	[11.0]	4.6	[3.0]	0.1	[0.07]	2.5	[0.2]
Vivianite	2.6	Bingham, Utah	Pale Purple	33.5	[16]	<0.4	[<0.2]				

[a] Approximate densities taken from literature, except that of cordierite which was measured.

[b] [M] = concentration in moles/liter.

enabled absorption measurements to be made parallel and perpendicular to the *a* direction, which corresponds to the trace of the 001 plane in the section.

Because the cordierite did not have easily identifiable cleavage or external morphology, a thin section was cut at random, and the principal optical directions were determined using a universal stage. This technique enabled the crystal to be oriented in such a way that sections containing principal optical directions could be cut. These were subsequently cut by the wire saw and ground to a suitable thickness. The correct optical orientations of the completed sections were confirmed by optical interference figures obtained with a petrographic microscope.

Measurement of spectra.

All spectra were measured at room temperature with a Beckman DK-2A recording spectrophotometer equipped with a sample holder having variable apertures for sample and reference beams.

Polarized spectra were obtained using either a pair of matched Nicol prisms or sheets of Polaroid film in the sample and reference beams. Experiment showed that the Polaroid film was ineffective as a polarizer at wavelengths longer than 800 mm.[1] Therefore, except where otherwise noted, the spectra in the infrared region were measured using Nicol prisms as polarizers.

The vibration direction, symbolized by $E \parallel$ or $E \perp$ to a specific crystallographic or optical direction, is marked on the appropriate spectra in the figures of this paper. Similarly UN refers to unpolarized spectra. Approximate extinction coefficients were calculated from the expression $\epsilon = A/C \times l$ where A is the absorbance at band maximum, C is the cation concentration in moles/liter and l is the thickness in cm. Net absorbance values were determined visually by assuming a gaussian distribution under each spectral feature, and, by taking into account the background absorption and possible overlapping of neighboring bands.

Minor vibrational bands in the infrared region of certain spectra have been deleted for clarity.

TOURMALINE

Structure of tourmaline.

Tourmaline, $Na(Mg, Fe, Mn)_3Al_6B_3Si_6O_{27}(OH, F)_4$, has a very complex structure (Donnay and Buerger, 1950), but for the purpose of explaining its absorption spectra it is necessary to consider only the disposition of the two kinds of sites containing octahedrally coordinated atoms, *i.e.* the (Mg, Fe, Mn)-site and the Al site.

As shown in Figure 1, the (Mg, Fe, Mn) ions lie in trigonal planes that are perpendicular to the *c*-axis. Each of these ions is surrounded by a nearly regular octahedron of four oxygen ions and two hydroxyl groups (omitted from Fig. 1 for reasons of clarity). These octahedra each share two edges with the adjoining octahedra in the trigonal plane, and two

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[1] In the original experimental work the authors unwittingly assumed that Polaroid film was effective in the infrared region. However, as pointed out by the referee of the present paper, this assumption was invalid. As a consequence most of the spectra were remeasured using Nicol prisms and certain corrections (mainly in intensities) were made. It is to be emphasized that these changes do not influence significantly the basic interpretations of the present work.

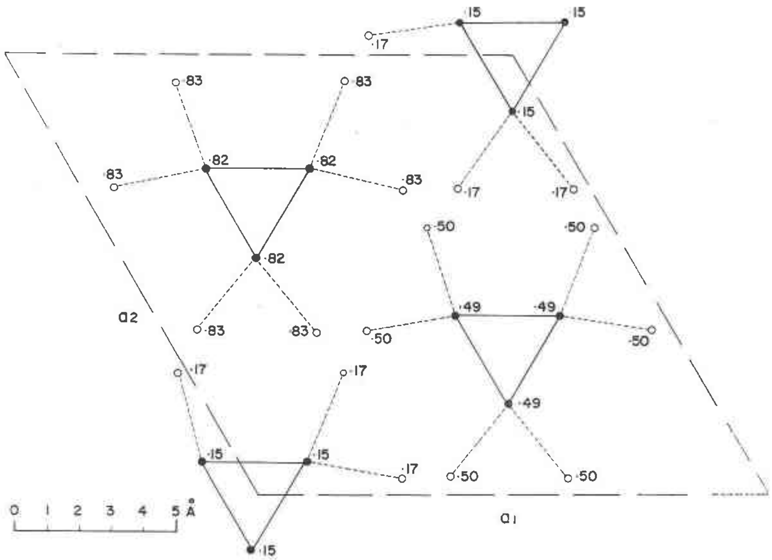

FIG. 1. A (001) projection of (Mg, Fe, Mn) ions (black circles) and Al ions (open circles) in tourmaline. Figures indicate fractional distances above the zero plane. Short metal-metal distances, representing directions across shared octahedral edges shown as solid lines between (Mg, Fe)-(Mg, Fe), and as dashed lines between (Mg, Fe)-Al.

edges with distorted Al-centered octahedra. These Al ions are displaced by 0.01–0.02 Å above the trigonal planes.

Each Al-centered octahedron also shares two edges with adjoining Al-centered octahedra, forming, in effect, spiral chains in the *c*-direction.

The absorption spectra of blue and green tourmalines.

Figures 2 and 3 show the polarized and unpolarized spectra of a dark-blue (*T-Bl-1*) and a medium-green (*T-Gr-1*) tourmaline, respectively. Except for spectrum *UN-2* in Figure 2, which is that of a basal (001) section of a blue tourmaline, the spectra are those of sections cut parallel to the *c* crystallographic axis (optic axis).

The spectra of green and blue tourmalines in the visible region are dominated by a pleochroic absorption band at ~14,000 cm^{-1}, while blue tourmalines also show a pleochroic band in the near-infrared at 9,000 cm^{-1}. Certain green tourmalines, on the other hand, show two pleochroic bands in the near-infrared, at 9,000 cm^{-1} in $E \perp c$ spectra and at 7,900 cm^{-1} in $E \| c$ spectra. Other green tourmalines, however, show only one important band in the near-infrared, at 9,000 cm^{-1} in $E \perp c$ spectra. Only the unpolarized spectra of the infrared region are shown in Figure 3.

The spectra are dominated by pleochroic absorption bands at ~14,000 cm^{-1} and ~9,000 cm^{-1}. These two features are typical of the spectra of

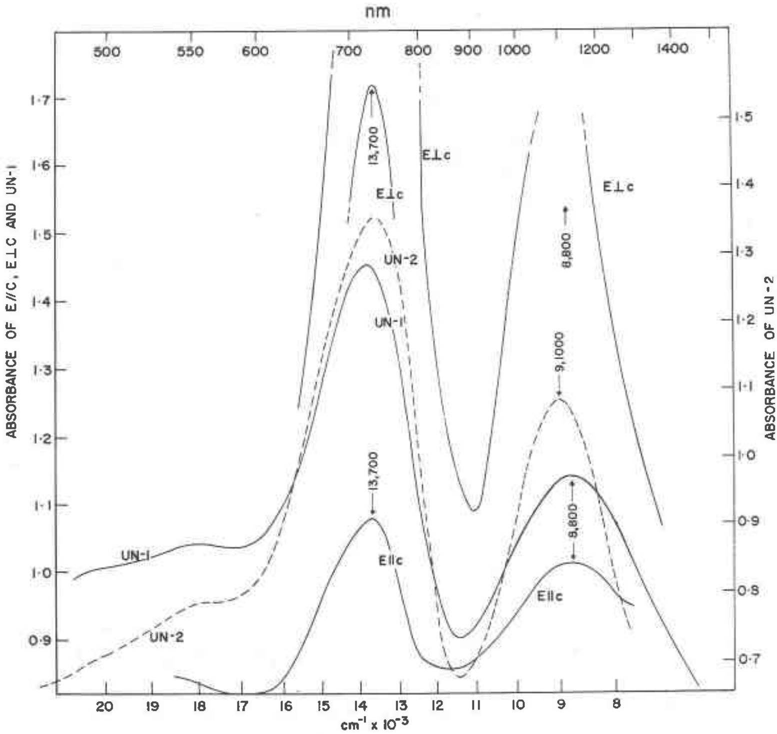

FIG. 2. Absorption spectra of tourmaline T-Bl-1. $E\|c$, $E\perp c$ and UN-1 are spectra of section cut parallel to *c*-axis, thickness 0.029 cm; UN-2 is unpolarized spectrum of a basal (001) section, thickness 0.012 cm.

all green-blue tourmalines examined in this laboratory. It is to be noted that the spectra of pink tourmalines differ greatly from those of Figures 2 and 3. However, this will be the subject of a future paper.

Because the high-energy limb of the ~14,000 cm^{-1} band extends into the visible region (25,000 − 14,000 cm^{-1}) its variation in intensity with changes in orientation of the mineral section in polarized light is an obvious cause of visible pleochroism. Such pleochroism also results from the pleochroic properties of the intense background (charge-transfer) absorbance sweeping into the visible from the ultraviolet region of the energy spectrum. This feature is much more pronounced in the spectra of *T-Gr-1* than in those of *T-Bl-1.*

Figure 4 shows the low-intensity features that appear in the unpolarized spectrum of a relatively thick section of *T-Bl-1.* These are similar in intensity, energy and number to those of vivianite, and other minerals of the present study containing appreciable amounts of ferrous iron. For comparison purposes the energy of the minor bands of tourmaline are

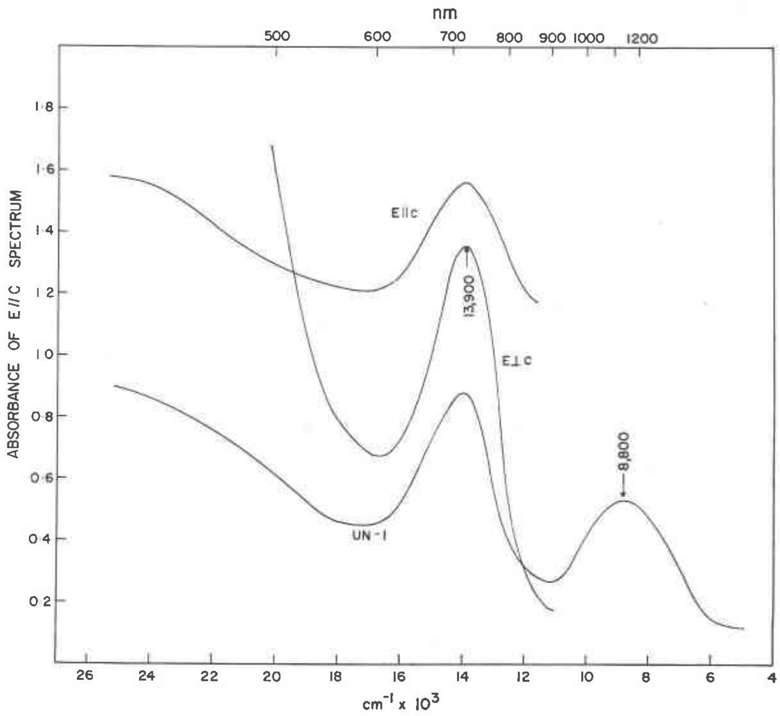

FIG. 3. Absorption spectra of tourmaline *T-Gr-1*. *E*∥*c*, *E*⊥*c* and *UN-1* are the spectra of a section cut parallel to the *c*-axis, thickness 0.05 cm. (Certain spectra shifted along absorbance scale for convenience of presentation.)

listed in Table 2 together with those of the other minerals; these will be discussed later in this paper.

Interpretation of spectra.

The origin of pleochroism.

The polarized spectra of Figure 2 and 3 are similar in several important respects to those of transverse (*i.e.*, ⊥001) sections of chlorite, biotite and phlogopite (Faye 1968). The spectrum of chlorite, for example, shows a highly pleochroic band at 14,300 cm^{-1} as well as pleochroic background absorbance originating in the ultraviolet region of the spectrum—these two features were shown to account for the intense visible pleochroism of the transverse sections of the minerals.

It was proposed (Faye 1968) that the pleochroic band at ~14,000 cm^{-1} in the sheet silicate spectra is due to "electron hopping" between Fe^{2+} and Fe^{3+} ions lying in the infinite planes of octahedrally coordinated cations. Such interaction was shown to be induced when the electric vec-

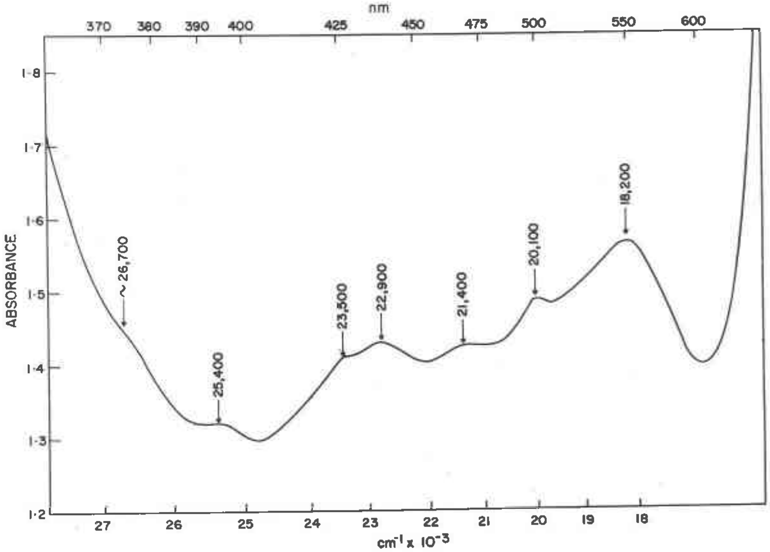

FIG. 4. Unpolarized spectrum of tourmaline T-Bl-1 showing low-intensity features due mainly to spin-forbidden transitions of Fe^{2+}, thickness of section ($\|c$-axis) 0.11 cm.

tor of the polarized light is in the same plane as the overlapping *d* orbitals of the t_{2g} set of Fe^{2+} and Fe^{3+} ions. Similarly, it was suggested that the pleochroic background absorbance might well be the result of $Fe^{2+} \rightarrow Al^{3+}$ interaction in the manner proposed by Burns (1966). It is reasonable then, to attempt to interpret the polarized spectra and pleochroism of the tourmalines in the manner that seemed to be successful for the sheet silicates.

From Figures 2 and 3 it is evident that the 13,700–13,900 cm^{-1} band is of maximum intensity (highest peak:background ratio) in the $E \perp c$ spectra, *i.e.*, when the electric vector of the incident light lies in the trigonal planes of the octahedrally coordinated (Mg, Fe) ions. This strongly suggests, as in the sheet silicates (Faye 1968), that the absorption band is due primarily to a photochemical oxidation-reduction process in which electron transfer is induced from Fe^{2+} ions in (Fe, Mg) sites to Fe^{3+} ions located in adjacent Al and/or (Fe, Mg) sites. Consideration of the orientation of the octahedral sites indicates that such a process could take place through overlapping *d* orbitals of the t_{2g} set of adjacent Fe^{2+} and Fe^{3+} ions. Of the 12 lobes of the d_{xy}, d_{yz} and d_{xz}[1] orbitals on each iron ion, a maximum of four are suitably oriented to participate in orbital overlap

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[1] Here x, y, z, refer to the Cartesian axes commonly used to denote the orientation of atomic orbitals and are not to be confused with the crystallographic axes.

TABLE 2. COMPARISON OF ENERGIES OF MINOR SPECTRAL FEATURES OF VIVIANITE, TOURMALINE, CORDIERITE AND CHLORITOID

Vivianite (Fig. 10)	Tourmaline T-Bl-1 (Fig. 4)	Madagascar Cordierite (Fig. 6c)	Chloritoid (Fig. 12)
26,300	~26,700	26,500	26,400
25,800	25,400	25,500	25,000
		24,800[a] (Fe^{3+}?)	
23,000	23,500	23,650	
22,000	22,900	22,800	22,400
20,750	21,400	21,600	21,800[a] (Fe^{2+} and/or Fe^{3+})
			21,000[a]
19,750	20,100	20,000	20,200
18,200	18,200	18,000[a] (Fe^{2+} and/or Fe^{3+})	19,400
		~17,000[a]	17,200[a] (Ti^{3+}?)

[a] Signifies spectral features that may be due to or influenced by transition-metal ions other than Fe^{2+}.

with neighbors. The remaining t_{2g} orbital lobes are not directed "end-on" at corresponding lobes on adjacent ions and consequently play no part in the pleochroism of tourmalines.

The ~14,000 cm^{-1} band is not present in the E ⊥001 spectrum of chlorite, for example (Faye, 1968), because the electric vector of the incident light is considered not to interact with overlapping *d*-orbital lobes. However, from Figures 2 and 3 it is apparent that the 13,700–13,900 cm^{-1} bands of the $E \| c$ spectra of the tourmalines have appreciable intensity, especially in those of the green tourmalines (Fig. 3). The ratio of the intensity of the 13,700 cm^{-1} band in $E \perp c$ and $E \| c$ spectra of blue tourmalines (Fig. 2) is obviously much higher than the ratio for green tourmalines. To account for this it seems necessary to assume that, where valency conditions are satisfied (perhaps F^- substituting for O^{2-}, for example), some Al^{3+} sites are occupied by Fe^{2+} ions and these can interact with adjacent Fe^{3+} ions in neighboring sites when the incident light is polarized parallel to the *c*-axis. Although the directions along which overlap would take place in such a scheme make angles of ~30° and ~150° with the *c*-axis, the projections of the overlapping orbitals along the *c*-axis are large, and therefore it is reasonable to expect significant interaction of polarized light with these oribtals. (It will be shown later that certain aspects of the polarized spectra of cordierite support the foregoing interpretations.)

The spectra of basal sections of the tourmaline (*e.g. UN-2* in Fig. 2) are nonpleochroic. This is to be expected because the electric vector of incident light polarized perpendicular to the *c*-axis has the same probability of interacting with overlapping Fe^{2+}–Fe^{3+} *d*-orbitals in all orientations of the mineral section.

In general, extinction coefficients (ϵ) for ligand→metal charge-transfer processes are greater than 10^3 liters/mole-cm (Drago, 1965, p. 151). Assuming that each Fe^{3+} ion can interact with a neighboring Fe^{2+}, then ϵ_{max} for the 13,700–13,900 cm^{-1} bands in the $E \perp c$ spectra of the two tourmalines are 100 liters/mole-cm (based on Fe^{3+} concentrations). If the Fe^{3+} or Fe^{2+} ions are clustered, however, the number of interacting Fe^{2+}–Fe^{3+} pairs is reduced, and the above ϵ-value of 100 will therefore be a minimum.

$^5T_2 \rightarrow {}^5E$ band of pseudo-octahedral Fe^{2+}.

Fe^{2+}, a d^6 ion, in an octahedral field gives rise to an absorption envelope due to the $^5T_2$ (^5D)→^5E (^5D) transition. In certain spectra this envelope is split by the dynamic Jahn-Teller mechanism for effect (Jahn and Teller 1937). It is well established that the $^5T_2 \rightarrow {}^5E$ band appears near 10,000 cm^{-1} in the spectra of Fe^{2+} in an octahedral environment of oxygens (Low and Weger, 1960; Cotton and Meyers, 1960; Burns, 1965;

Jones, 1967). Although the energy of the 8,800–9,100 cm^{-1} band in the spectra of tourmaline *T-Bl-1* for example (Fig. 2) seems somewhat low, it is necessary to assign it to the $^5T_2 \rightarrow {}^5E$ transition, if for no other reason than because it is the only ion present in sufficient concentration (2–3 M) in the tourmaline to account for the band.

It is noteworthy that the 8,800–9,100 cm^{-1} band in *T-Bl-1* does not appear to be split by the Jahn-Teller mechanism in the manner of the sheet silicates and vivianite (Faye 1968). This suggests that the relatively rigid lattice of tourmaline does not permit the necessary vibrational distortions for the Jahn-Teller effect to be observed.

As mentioned earlier, certain green tourmalines exhibit two bands in the near infrared, at 9,000 cm^{-1} in $E \perp c$ spectra and at 7,900 cm^{-1} in $E \| c$ spectra. Because the (Mg, Fe^{2+}) sites in green and blue tourmalines are unlikely to be different, it seems reasonable to assign the 9,000 cm^{-1} band to Fe^{2+} in the trigonal units. The 7,900 cm^{-1} band, with maximum intensity in $E \| c$ spectra, can therefore be assigned to Fe^{2+} located in the Al^{3+} positions in the spiral chain. The presence of two bands in the near-infrared spectra of green tourmaline is consistent with the very appreciable intensity of the 13,900 cm^{-1} band in $E \| c$ spectra.

The pleochroism of the 8,800 cm^{-1}–9,100 cm^{-1} band in the blue tourmaline (Fig. 2) may be due to preferential electron occupation of the t_{2g} orbital lobes lying in the plane of the trigonal units. Alternatively, the pleochroism may be a manifestation of differing degrees of vibronic coupling of electronic and vibrational states in the $E \| c$ and $E \perp c$ directions. It will be seen that such a mechanism is invoked to explain the pleochroism of a corresponding band in the spectra of cordierite.

During the preliminary examinations of a number of tourmaline sections that were cut parallel to the *c*-axis, it was observed that the maximum of the $^5T_2 \rightarrow {}^5E$ band shifted to higher energies as the sections were thinned. This suggests that the strength of the crystal field increases as the thickness of the tourmaline section is decreased. Although the reason for the increasing strength of the ligand field is not known, an increase could occur if the Fe^{2+}-(O, OH) bond distances become shorter due to lattice contraction.

Origin of the 24,000 cm^{-1} band in green tourmalines and the color of *T-Bl-1* and *T-Gr-1*.

The spectra of green tourmalines (Fig. 3) show a pleochroic absorption band (shoulder) at 24,000 cm^{-1}, with maximum intensity in $E \perp c$ spectra. This band is not observed in the spectra of blue tourmalines (Fig. 2), and it is apparent that the band largely accounts for the difference in color between green and blue tourmalines. The ~24,000 cm^{-1} band is not resolved in the $E \perp c$ spectrum in Figure 3, but its presence is obvious from UN-1 and $E \| c$ spectra.

The 24,000 cm^{-1} band could be due to Ti^{3+}–Ti^{4+} interaction in the 001 plane. A pleochroic band at 23,000 cm^{-1} in $E \perp 001$ spectra of the sheet-silicate astrophyllite coincides with the orientation of the linear Ti-O-Ti units (unpublished work in these laboratories) in which Ti is a major constituent. Faye (1968) has also associated a band at ~24,000 cm^{-1} in biotite spectra with the presence of Ti. Assigning the ~24,000 cm^{-1} band in green tourmalines to Ti would therefore seem reasonable.

The spectra of tourmaline *T-Gr-1* (Fig. 3) clearly show that the low energy limb of the 24,000 cm^{-1} band sweeps into the visible portion of the spectrum and absorbs violet and blue light. The Fe^{2+}–Fe^{3+} band centered at 13,900 cm^{-1} absorbs red light, and the combined effect, therefore, is to give specimen *T-Gr-1* a green color. The spectra of *T-Bl-1* (Figs. 2 and 4) show that red light is absorbed by the high-energy limb of the 13,700 cm^{-1} band and yellow-green light by the minor features between 425 and 550 nm. The net effect is to give a specimen of modest thickness (e.g. 0.1 cm) a dark-blue color. It will be seen later, under vivianite, that most of the low-intensity bands and shoulders are considered to be due to spin-forbidden transitions in six-coordinate Fe^{2+}.

It is to be emphasized that the processes involved above for the coloration of the blue and green tourmaline do not apply to pink tourmalines.

CORDIERITE

The structure of cordierite.

Figure 5 shows the structure of cordierite, $Mg_2Al_3AlSi_5O_{18}$, projected on 001 (Byström 1942). Later structural analyses have resulted in relatively minor modifications of this structure, but the essential structural elements have been shown to be correct (Gibbs 1966). In the unit cell there are two layers, 3.74 Å apart, of oxygen-linked, four- and six-coordinate cations parallel to 001 and separated by a layer of (Si, Al)O_4 tetrahedra. It is accepted that Fe^{2+} and Mn^{2+} may substitute for Mg^{2+} in the octahedral sites and that Fe^{3+} may proxy for Al^{3+} in certain of the tetrahedral sites (Deer, Howie and Zussman, 1962).

Although the six Mg-O bond lengths of the Mg site are practically equal (2.11–2.12 Å), the bond angles vary from 71° to 102° (Gibbs, 1966); therefore the true site symmetry must be lower than O_h. However, as we will see later, the spectra indicate that the (Mg, Fe) coordination polyhedron may be treated as a nearly regular octahedron.

There are five kinds of (Si, Al)O_4 tetrahedra in cordierite but, according to Gibbs, only the larger two of these are preferentially occupied by Al^{3+}. In one of these tetrahedra (T_1), Al^{3+} ions lie in the same planes as the Mg^{2+} ions. Each Mg^{2+} octahedron shares an edge with each of two of the T_1 tetrahedra, as well as an edge with one of the small tetrahedra (T_2) in which the Al^{3+} occupancy is considered to be low (see Fig. 5).

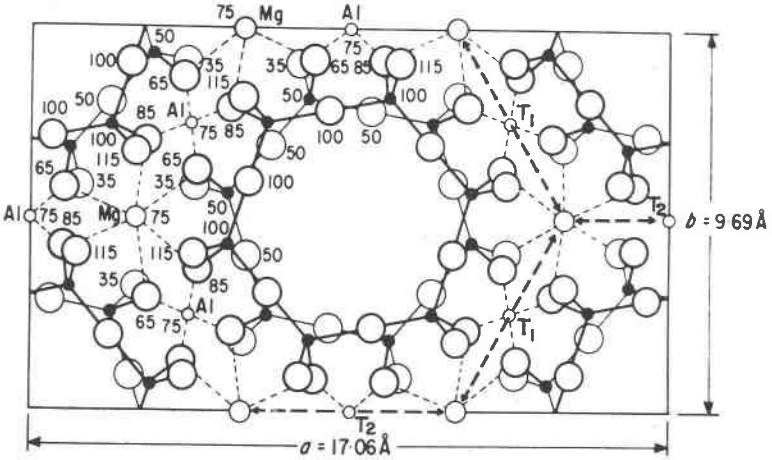

FIG. 5. Structure of cordierite viewed down the *c*-axis (after Bystrom, 1942). The directions in which orbital overlap is considered to occur between octahedrally coordinated Fe^{2+} ions and tetrahedrally coordinated Fe^{3+} ions (T_1 and T_2) is indicated by heavy dashed arrows.

Polarized absorption spectra of oriented sections of cordierite.

The polarized spectra of *a-b*, *a-c* and *b-c* sections of Madagascar cordierite are shown in Figure 6. The direction of vibration of the electric vector of light (E) is indicated in each spectrum.

A common feature of the spectra of Figure 6 is a pleochroic band system centered between 8,000 and 11,000 cm^{-1}. The 10,750 cm^{-1} component of this system in the $E||b(Z)$ spectra is appreciably more intense than in the $E||a(Y)$ and $E||c(X)$ spectra. Because the high-energy wing of the 10,750 cm^{-1} band does not penetrate into the visible region of the spectrum, it does not contribute to the color of cordierite.

From Figure 6 it is apparent that there is a broad pleochroic absorption envelope centered at approximately 17,500 cm^{-1} (570 nm) in the spectra of all three crystallographic sections. This band has its maximum intensity in the $E||a$ spectra of the *a-c* and *a-b* sections and has no intensity in the $E||c$ spectra of *a-c* and *b-c* sections. Because the 17,500 cm^{-1} band is located in the visible region of the spectrum, it is obvious that its polarization properties largely account for the visible pleochroism of cordierite.

A number of minor features, indicated by arrows, are superimposed on the broad polarized band in the $E||a$ spectrum of Figure 6(c). They are also present, but less obvious, in all the other spectra of Figure 6. Because of their low intensity they do not contribute significantly to the color of

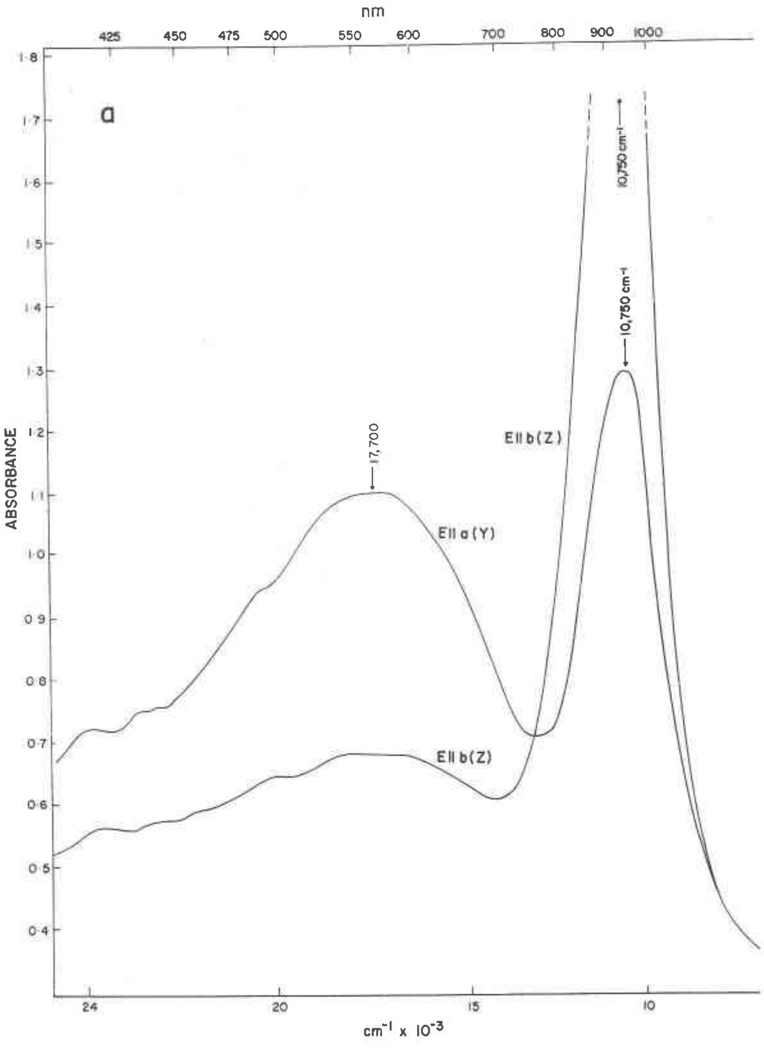

FIG. 6. (a) Polarized spectra of an $a(=Y)$-$b(=Z)$ section of cordierite; thickness 0.20 cm.

the cordierite. The energy of these minor bands is listed in Table 2, where they are compared with similar features in the spectra of vivianite, tourmaline and chloritoid.

Interpretation of spectra.

$^5T_2 \rightarrow {}^5E$ band of pseudo-octahedral Fe^{2+}.

Although the Madagascar cordierite was analyzed only for Fe^{2+}, Fe^{3+}

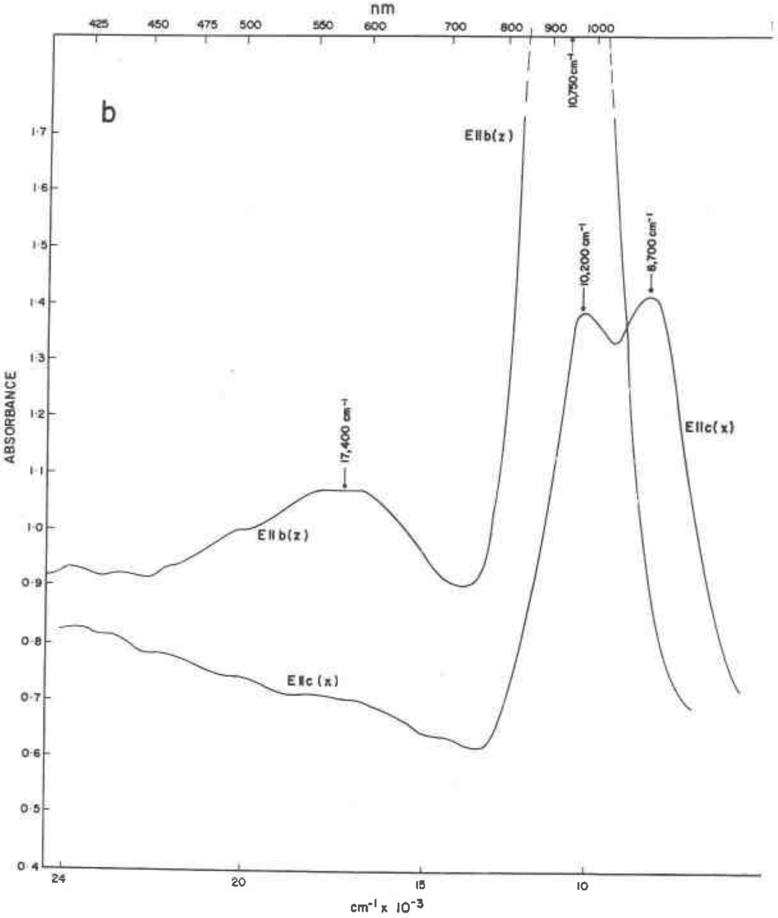

FIG. 6. (b) Polarized spectra of a *b*(Z)-*c*(X) section of cordierite; thickness 0.26 cm.

and total Mn (Table 1), it can be assumed that other transition-metal ions are not present in sufficient concentration to influence the absorption spectra of the specimen (Deer, Howie and Zussman 1962, pp. 276–278). Because Fe^{2+} is the principal transition-metal ion in the cordierite, it is proposed that the band system centered between 8,000 and 11,000 cm^{-1} in the spectra of Figure 6 is due to the $^5T_2 \rightarrow {}^5E$ transition of Fe^{2+} in pseudo-octahedral (Mg^{2+}) sites. Such an assignment is consistent with that made previously in this paper for tourmalines and for other silicate minerals (*e.g.* Burns 1965; White and Keester, 1966; Faye, 1968).

Unlike the $E\|a$ and $E\|b$ spectra which show only a single band at

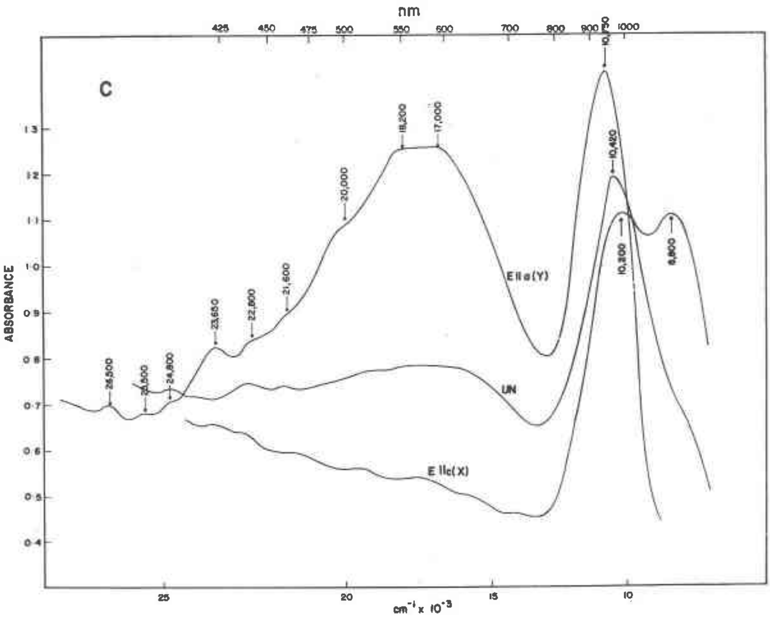

FIG. 6. (c) Polarized spectra of an *a*(Y)-*c*(X) section of cordierite; thickness 0.19 cm.

10,750 cm^{-1}, the $E\|c$ spectrum has two prominent bands at 10,200 and 8,800 cm^{-1}. This splitting may be due to the dynamic Jahn-Teller mechanism as in the sheet silicates and vivianite (Faye 1968a) or, to a modest static distortion of the Fe^{2+} site from O_h symmetry. However, in the latter case it is difficult to explain why the splitting should be appreciable only in the $E\|c$ spectrum.

That the $E\|b$ spectrum is notably more intense than the $E\|a$ and $E\|c$ spectra may be due to enhanced vibronic coupling in the *b*-crystallographic direction. Such an argument is not inconsistent with the proposal that the $E\|c$ spectrum is split by the dynamic Jahn-Teller mechanism.

Pleochroism and $Fe^{2+}{}_{oct}\rightarrow Fe^{3+}{}_{tet}$, interaction.

From Figure 6 it is readily apparent that the pleochroism and polarization properties of the band at ~17,500 cm^{-1} are related to the orientation of the planes of cations in which transition-metal ions may substitute. This immediately suggests, as in the case of tourmaline, that the polarized band is due to the electronic interaction (in polarized light) of Fe^{2+} and Fe^{3+} ions through *d*-orbital lobes that lie in planes parallel to 001. However, in contrast to the octahedral-octahedral interaction in tourmaline and the sheet silicates, it is necessary to propose that, in cordierite, orbital overlap may occur between favorably oriented *d*-orbital lobes (a maximum of three of twelve) of the t_{2g} set of octahedrally coordinated Fe^{2+}, and a maximum of two of six lobes of the e_g set ($d_{x^2-y^2}$ and d_{z^2}) of tetrahedrally coordinated Fe^{3+}. The directions in which this overlap is expected to occur all lie in the 001 plane, and are shown in Figures 5 and 7.

Since light polarized parallel to *a* coincides with the direction of overlap in several places in Figure 5, it can readily be appreciated that the $\sim$17,500 cm^{-1} band should have maximum intensity in the $E||a$ spectra. Figure 6 shows that this is the case. The intensity of this band in the $E||b$ spectra is lower, as expected, because there are no overlap directions coinciding with *b*; nevertheless, this band is perceptible in these directions probably because the angle between some of the overlap directions and the *b*-direction is not large. On the other hand, the $\sim$17,500 cm^{-1} band has no measurable intensity when $E||c$; this is to be expected from the fact that there are no overlapping orbitals in the *c*-direction.

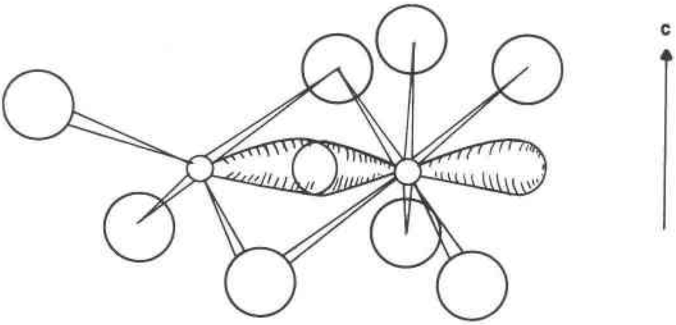

FIG. 7. A highly diagrammatic representation of the overlapping of an *eq* orbital lobe of a tetrahedrally coordinated Fe^{3+} ion with a t_{2g} orbital lobe of an octahedrally coordinated Fe^{2+} ion in cordierite.

Although a satisfactory explanation cannot be given at this time, it is significant to note that $Fe^{2+}{}_{oct} \rightarrow Fe^{3+}{}_{tetr}$ interaction in cordierite results in a broader band of higher energy ($\sim$17,500 cm^{-1}) than does $Fe^{2+}{}_{oct} \rightarrow Fe^{3+}{}_{oct}$ interaction ($\sim$14,000 cm^{-1}) in green-blue tourmalines and certain sheet silicates (Faye 1968).

The apparent extinction coefficient for the 17,500 cm^{-1} band, calculated on the basis of every Fe^{3+} ion interacting with an Fe^{2+} ion, is approximately 20 liter/mole-cm. This value is significantly lower than that calculated ($\sim$100 liter/mole-cm) for the corresponding $Fe^{2+}-Fe^{3+}$ interaction bands of certain sheet silicates (Faye 1968) and the tourmalines. However the total iron concentration of the cordierite is appreciably lower than the other minerals and thus the concentration of interacting species is also lower.

The polarized absorption spectra of cordierite have been examined recently by Newnham and Farrell (1967), but their interpretation is not consistent with that proposed in this paper. Newnham and Farrell argued that the bands at ~17,000 and ~10,000 cm^{-1} in their spectra were both due to *d-d* transitions of Fe^{2+} in a distorted octahedron having orthorhombic symmetry. While a highly distorted site could result, theoretically, in the spectral appearance of two or more bands separated by 6,000–7,000 cm^{-1}, such an explanation would not seem to be valid for the spectra of cordierite. It is significant that the "center of gravity" of the visible and infrared band systems is approximately 14,000 cm^{-1}, a value unusually high for six-coordinate Fe^{2+} in an oxygen environment.

VIVIANITE

The structure of vivianite.

Figure 8 (after Mori and Ito, 1950) shows the orientation of the Fe-bearing coordination polyhedra in vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) as viewed from approximately the *b*-direction. Since vivianite has perfect 010 cleavage, this representation corresponds to that of a cleavage plate. According to Mori and Ito (1950) there are two kinds of nearly regular octahedral sites in the lattice. In one site (Fe_I) the Fe^{2+} ion is coordinated by

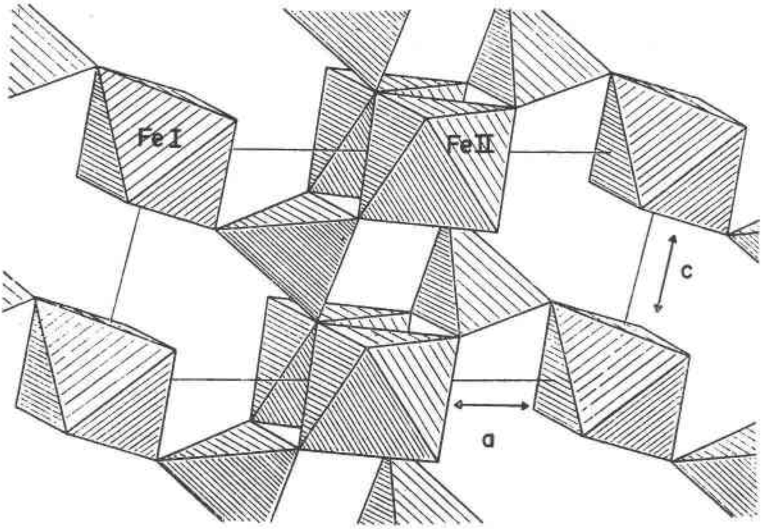

FIG. 8. Diagrammatic representation of an *a-c* cleavage tablet of vivianite showing the Fe_I and Fe_{II} sites (after Mori and Ito, 1950).

four H_2O's in a plane and by two trans-oxygen atoms (from PO_4^{3-} units); in the other site (Fe_{II}) two H_2O's are coordinated in a cis arrangement and the remaining sites are occupied by oxygens. Two Fe_{II} octahedra sharing a common O-O edge straddle the *a*-crystallographic axis.

Polarized absorption spectra of oriented sections of vivianite.

Figure 9(a) shows the spectra of a section cut to contain the optical directions X and Z, while Figure 9(b) shows the spectra of a section cut to contain the X and Y directions. Because the spectra of Figure 9 were measured with Polaroid film they are essentially unpolarized at wavelengths higher than 800 nm. Figure 10 shows the unpolarized spectrum of an *a–c* (010) cleavage tablet of vivianite.

In most of the spectra of Figures 9 and 10, two bands (shoulders) appear in the 8,200–12,000 cm^{-1} region. In the spectra of Figure 9(b) especially, these features are very similar to corresponding bands in the spectra of certain sheet silicates (Faye, 1968, 1968a). Because the high-energy wing of the 10,900–12,000 cm^{-1} band does not reach into the visible region (25,000–14,000 cm^{-1}) except in thick sections, it does not contribute to the color of vivianite.

The most remarkable feature of the spectra of Figure 9 is unquestionably the very intense and incompletely resolved band that has its maximum (by inference) between ~15,000–16,000 cm^{-1}. This band has its maximum intensity in the $E\|b(X)$ spectra of sections that have been partially oxidized in the thinning processes and does not have measurable intensity in the $E\perp b(Y \text{ or } Z)$ spectra of such sections. There is no doubt that the polarization properties of the band at 15,000–16,000 cm^{-1} are responsible for the intense pleochroism of vivianite that has been partially oxidized.

The minor features appearing in the visible region of the spectrum are clearly resolved in Figure 10. The energies of these bands and shoulders are listed in Table 2 where they are compared with similar ones found in the spectra of tourmalines, cordierite and chloritoid.

Interpretation of the spectra of vivianite.

The unpolarized spectrum (7,000–30,000 cm^{-1}) of an *a–c* cleavage tablet of vivianite (Fig. 10) has been interpreted previously (Faye 1968). It was proposed that the double-band system in the 8,000–12,000 cm^{-1} region was the result of the dynamic Jahn-Teller mechanism (Cotton and Meyers, 1960; Jones 1967) acting on Fe^{2+} in a nearly regular octahedral crystal field. Obviously the same interpretation must apply to the corresponding bands in the spectra of Figure 9.

With respect to the spectra of Figure 9 and 10, it is interesting to note

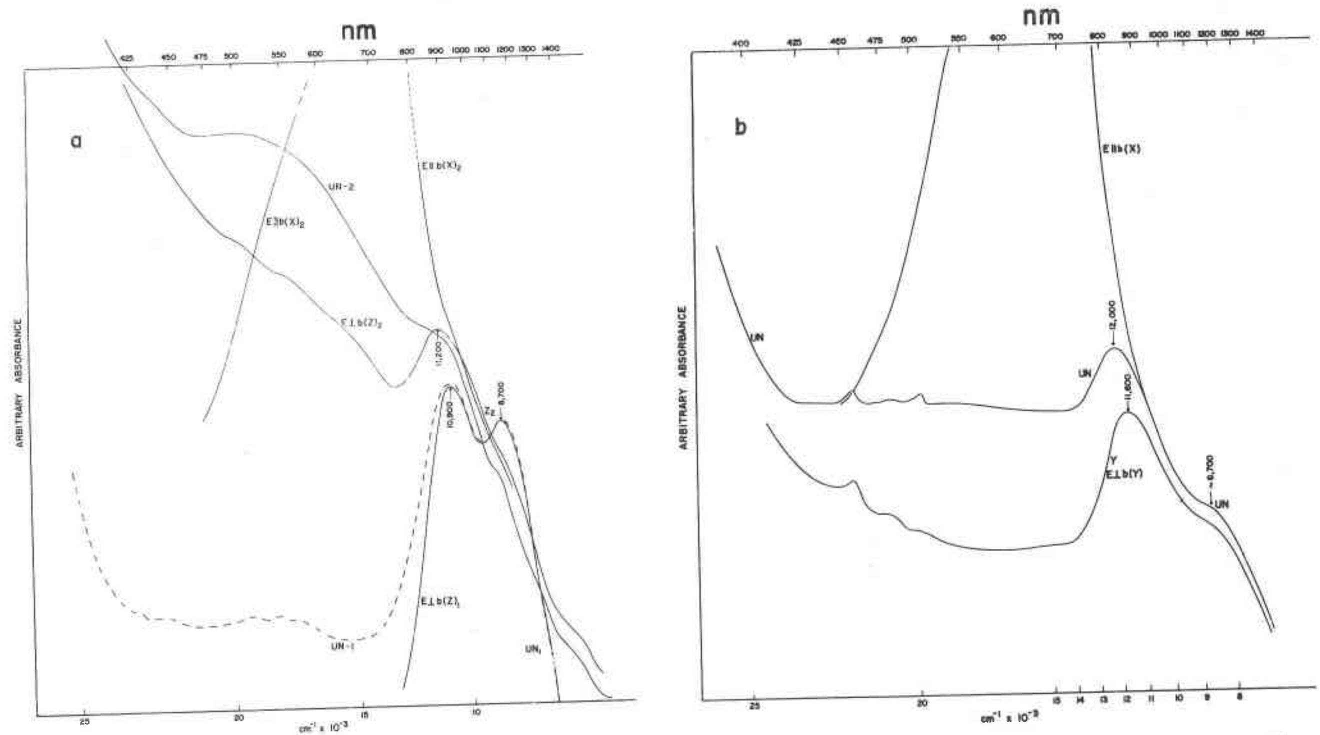

FIG. 9. (a) Absorption spectra of *X-Z* sections of vivianite. E$\perp b(Z)_1$, and *UN*-1 spectra of section having a thickness of 0.013 cm E$\|b(X)_2$, E$\perp b(Z)_2$ and *UN*-2 spectra of section of thickness 0.007 cm. (b) Absorption spectra of an *X-Y* section of vivianite; thickness of 0.007 cm. Note: Vivianite spectra measured in unpolarized light below ~12,000 cm^{-1}.

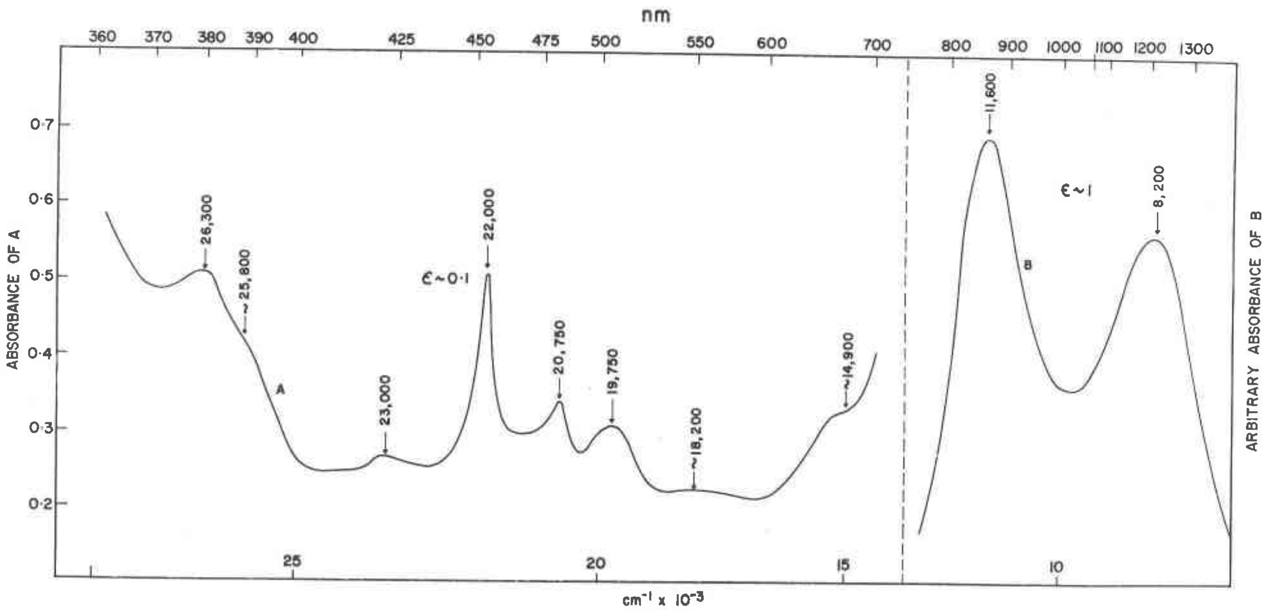

FIG. 10. Unpolarized spectrum of an *a-c* cleavage tablet of vivianite. A. thickness 0.14 cm; B. thickness 0.035 cm.

that the band splitting due to the dynamic Jahn-Teller mechanism is greatest in that of an *a–c* cleavage tablet. This suggests that the vibrational modes inducing the distortions of the Fe^{2+} sites have their greatest amplitude in the *a–c* plane.

$Fe^{2+} \rightarrow Fe^{3+}$ interaction in partially oxidized vivianite.

Freshly mined vivianite is colorless or has a superficial pale blue color near fracture or cleavage surfaces. On grinding, however, as in the thinning of the crystallographically oriented sections used to obtain the spectra of Fig. 9, the mineral acquires a blue color and a correspondingly intense pleochroism. Unquestionably some ferrous iron is oxidized during such processes and this establishes the condition for the $Fe^{2+} \rightarrow Fe^{3+}$ interaction along directions in which there is overlap of favorably oriented lobes of t_{2g} orbitals of adjacent ions.

Thus the intense absorption band at 15,000–16,000 cm^{-1} in the $E \| b(X)$ spectra of Figure 9 can easily be explained on the same basis as the polarized bands at $\sim$14,000 cm^{-1} and 17,500 cm^{-1} in the spectra of tourmaline and cordierite, respectively.

In vivianite it is necessary to conclude that the $Fe^{2+} \rightarrow Fe^{3+}$ interaction occurs between ions only in adjacent Fe_{II} sites (Mori and Ito, 1950) along the *b*-direction because distances are too great for interactions of the $Fe_I^{2+} \rightarrow Fe_I^{3+}$ or $Fe_I^{2+} \rightarrow Fe_{II}^{3+}$ type in the *c* and *a* directions, respectively.

It is of interest to note that on each interacting iron ion, only one of twelve t_{2g} orbital lobes can participate in overlap with a neighbour, namely the one directed across the shared octahedral edge. Despite the more limited orbital-overlap possibilities between Fe^{2+} and Fe^{3+} ions in partially oxidized vivianite, the probability of interaction is much higher than in tourmalines and cordierite, for example, because iron is the principal constituent in the former and usually a minor one in the latter minerals. Therefore, it is readily understandable that for a mineral section of a given thickness, the intensity of the absorption band due to the $Fe^{2+} \rightarrow Fe^{3+}$ interaction in the vivianite spectra will probably be much higher than in ferromagnesian silicates. Making the assumption that ϵ for the Fe^{2+}-Fe^{3+} interaction band of vivianite is as low as 100 liter/mole-cm and using a very approximate value ($\sim$3 units) of the absorbance of the $E \| b(X)_2$ spectrum of Figure 9(a), for example, it can be calculated that the Fe^{3+} concentration is approximately 3 M, some 20 percent of the total iron. This value is probably unrealistically high because of the low ϵ-value used. Vivianite containing such a concentration of ferric iron would probably show a brown color because of intense background absorption due to the $O^{2-} \rightarrow Fe^{3+}$ charge-transfer process.

Comparison of minor features in the visible spectrum of vivianite with those of tourmaline, cordierite and chloritoid.

The unpolarized spectrum of unoxidized vivianite has been studied previously (Faye 1968a). The well-resolved low-intensity bands and shoulders (see Fig. 10) in the 15,000–10,000 cm^{-1} region were all assigned to spin-forbidden transitions (quintuplet to triplet and singlet states) of octahedrally coordinated Fe^{2+}. Such an assignment scheme seems unequivocal because only Fe^{2+} is present in sufficient concentration in vivianite to give measurable spectral features (Table 1).

Previously in this paper, reference was made to the minor features that appear in the visible region of the spectra of tourmaline *T-Bl-1* and cordierite. Although these minerals contain significant concentrations of Fe^{3+} and/or other transition-metal ions as well as Fe^{2+} (Table I), it is reasonable to compare their spectra with that of vivianite in an attempt to assign the bands and shoulders due to spin-forbidden transitions of pseudo-octahedrally coordinated Fe^{2+}. Accordingly, Table 2 lists the energies of the bands and shoulders in the 15,000–30,000 cm^{-1} region of the spectra of vivianite, tourmaline *T-Bl-1*, cordierite and chloritoid and indicates those that are considered to be due to such transitions and those that may be due to, or influenced by, other transition-metal ions (*e.g.* Fe^{3+}, Mn^{2+}, Mn^{3+}, Ti^{3+}). Although the structure and spectra of chloritoid (Fig. 11) are to be discussed in the next section of this paper, it is convenient here to tabulate and compare the low-intensity features that can be ascribed to spin-forbidden transitions of Fe^{2+}, with those of the other minerals.

Although the energy of the $^5T_2 \rightarrow {}^5E$ transition (10 Dq) of Fe^{2+} varies, somewhat from mineral to mineral (see Figs. 2, 3, 6, 9, 12) because of its marked dependence on the strength of the crystal field, certain of the spin-forbidden transitions discussed above are much less field-dependent (Burns 1965), and it is therefore understandable that their energies would be similar in the spectra of the suite of minerals under consideration.

CHLORITOID

The structure of chloritoid, $Fe_2Al_4(OH)_4Si_2O_{10}$.

The structure of chloritoid can be expressed in terms of two layers of octahedrally coordinated cations: one a brucite type, having the composition (Fe^{2+}, Mg)$_4$Al$_2$O$_8$(OH)$_8$, the other a corundum-type, of composition Al_6O_{18}. These sheets alternate in the direction parallel to the (001) plane and are linked by layers of SiO$_4$ tetrahedra, also parallel to the basal plane, and by hydrogen bonds (Deer, Howie and Zussman 1962, p. 163). Figure 11 shows part of the chloritoid structure projected on (010) after Brindley and Harrison (1952).

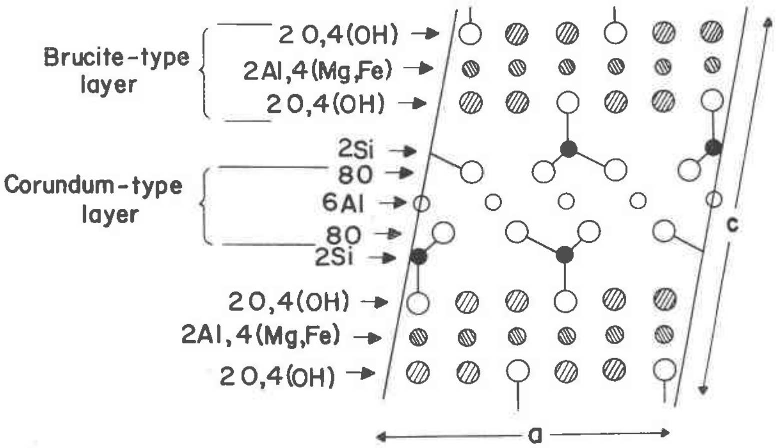

FIG. 11. Part of the chloritoid structure projected on (010) plane (after Brindley and Harrison, 1952).

Interpretation and discussion of the $E\|a$ and $E\perp a$ spectra of a transverse section of chloritoid.

Figure 12 shows the $E\|a$ and $E\perp a$ spectra of a transverse section of chloritoid. The relatively minor differences between the two spectra can be attributed to the fact that the background absorption of $E\|a$ is somewhat more intense than in $E\perp a$.

The bands (shoulders) at 8,300 and 11,500 cm^{-1} correlate directly with the two-band system in the 8,200–12,000 cm^{-1} region of the vivianite spectra discussed earlier and also with that in the spectra of the sheet silicates muscovite (Faye 1968a), chlorite, phlogopite and biotite (Faye 1968). These two features have been attributed to the dynamic Jahn-Teller splitting of the upper state in the $^5T_2 \rightarrow ^5E$ transition of Fe^{2+} in pseudo-octahedral sites.

The low-intensity shoulders in the visible portions of the spectra of Figure 11 have previously been discussed and are tabulated in Table 2. Most of these are probably due to spin-forbidden *d-d* transitions of octahedrally-coordinated Fe^{2+}.

There is some uncertainty about the origin of the broad band with its maximum at ~17,200 cm^{-1}. Because it is not pleochroic, it probably cannot be ascribed to the same process invoked for the pleochroic band at similar energy in the spectra of cordierite, *i.e.*, iron-iron interaction. It may be a *d-d* band of a transition-metal ion other than Fe^{2+}, possibly Ti^{3+}.

Table 2 shows that the Urals chloritoid specimen contains 2.5 percent Ti; therefore it is suggested that the prominent band at ~17,200 cm^{-1}

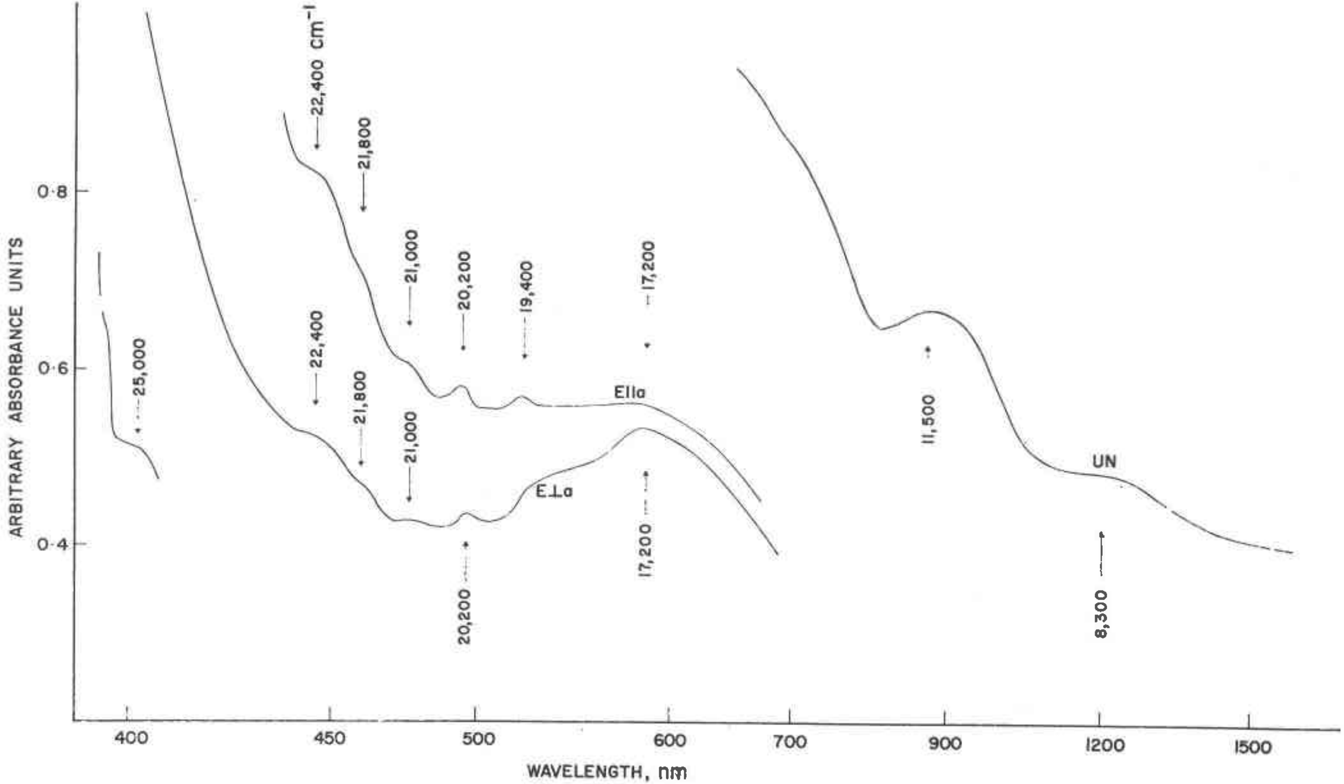

FIG. 12. Polarized spectra of a transverse section of chloritoid; thickness 0.005 cm. Note: Chloritoid spectrum measured in unpolarized light below ~12,000 cm⁻¹.

($\epsilon \sim 30$ liter/mole-cm) in its spectrum may represent the $^2T_2 \rightarrow {}^2E(D)$ transition of pseudo-octahedrally coordinated Ti^{3+}. This assignment is supported by the 17,200 cm^{-1} band also present in the spectrum of a chloritoid from Rhode Island that contained 5 percent Ti. A strong absorption band at 19,000 cm^{-1} in andradite spectra has earlier been assigned to octahedrally bonded Ti^{3+} (Manning, 1967).

Perhaps the most important aspect of the chloritoid spectra is the absence of a pleochroic band in the 14,000–18,000 cm^{-1} region which could signify $Fe^{2+} \rightarrow Fe^{3+}$ interaction of the type proposed previously for other minerals in this paper. From a structural standpoint, there should be considerable opportunity for iron-iron interaction parallel to 010 since there is abundant sharing of octahedral edges in this plane, both in the brucite and in the corundum layers. That there is no spectral evidence for such interaction, even though the concentrations of Fe^{2+} ($\sim$10 M) and Fe^{3+} ($\sim$3M) in the chloritoid are appreciable, suggests that these divalent and trivalent cations are not suitably located relative to each other for orbital overlap. Such a condition would exist if the cations were segregated in separate layers, *e.g.* Fe^{3+} in the corundum layer, and Fe^{2+}, as might be expected, in the brucite layer. Indeed, it has been suggested that Fe^{3+} can replace Al^{3+} in chloritoid up to 10 atomic percent (Halferdahl, 1957). The apparent replacement in the specimen under consideration would seem to be within this limit.

Thus it is considered that the negative evidence inherent in the polarized spectra of chloritoid is not inconsistent with the proposed role of $Fe^{2+} \rightarrow Fe^{3+}$ interaction in the pleochroism of the minerals considered previously in this paper.

CONCLUSIONS

Although it has been speculated for years (Weyl, 1951; Martinet and Martinet, 1952) that the pleochroism and color of many silicate minerals was somehow influenced by the simultaneous presence of Fe^{2+} and Fe^{3+}, a satisfactory explanation of their roles has not been made prevously.[1] This

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[1] At the time of submission of this manuscript to the American Mineralogist the authors were unaware of two articles that had been published in *Progress in Inorganic Chemistry*, Vol. 8, 1967 and which bear directly on the intervalence charge-transfer interaction and their spectral effects: "Intervalence-Transfer Absorption. Part I. Qualitative Evidence for Intervalence-Transfer Absorption in Inorganic Systems in Solution and in the Solid State," by G. C. Allen and N. S. Hush, p. 357; and "Intervalence-Transfer Absorption. Part 2. Theoretical Considerations and Spectroscopic Data," by N. S. Hush, p. 391.

Although the $Fe^{2+} \rightarrow Fe^{3+}$ interaction in vivianite and in other materials is treated by the above authors, their approach is somewhat different to that of the present paper. The two works complement and support each other, and emphasize the importance of the so-called intervalence effects.

is understandable because only through the use of recently developed crystal- or ligand-field theory has it been possible to propose reasonable mechanisms for the interaction of transition-metal ions with electromagnetic radiation.

The present work shows that pleochroic, or polarized, absorption bands may be present in the visible spectrum of a mineral (especially ferromagnesian silicates) when adjacent Fe^{2+} and Fe^{3+} ions are so located in the lattice that certain of their *d*-orbital lobes may overlap in planes that are parallel to one or more crystallographic axes. In these spectra the polarized light lies in the same plane(s) as the overlapping *d*-orbitals. Conversely, such bands will have no intensity when the vibration direction of the light is perpendicular to the plane(s) containing overlapping *d*-orbitals.

Of the minerals studied in the present work, it is convenient to think of partially oxidized vivianite as one extreme in which there is maximum probability of $Fe^{2+} \rightarrow Fe^{3+}$ interaction and chloritoid as the other extreme in which there is little evidence of such interaction. Green-blue tourmalines and cordierite obviously represent intermediate cases in which their pleochroism is largely dependent on the probability of the $Fe^{2+} \rightarrow Fe^{3+}$ interaction, which, in turn, must depend on the concentrations of Fe^{2+} and Fe^{3+} and the ratio of these concentrations.

Because Fe^{2+} and Fe^{3+} are ubiquitous in ferromagnesian minerals, it is reasonable to suggest that with a knowledge of the structure of a mineral and its approximate content of Fe^{2+} and Fe^{3+}, one might well be able to predict the possibility of an $Fe^{2+} \rightarrow Fe^{3+}$ interaction band influencing its spectrum. Conversely, the results of optical absorption studies may be able to provide information on the valence states of iron atoms in the mineral and their distribution within the structure.

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