THE OPTICAL ABSORPTION SPECTRA OF IRON IN SIX-COORDINATE SITES IN CHLORITE, BIOTITE, PHLOGOPITE AND VIVIANITE. SOME ASPECTS OF PLEOCHROISM IN THE SHEET SILICATES

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Abstract

The electronic absorption spectra of the sheet silicates, chlorite, biotite and phlogopite and the ferrous phosphate, vivianite, have been measured in the 7,000–30,000 cm^{-1} region. Interpretations have been made of some aspects of the structure, colour and pleochroism of certain of these materials.

The complex spectra of chlorite and biotite in the visible region show similarities to that of vivianite, a mineral known to contain Fe^{2+} in nearly regular octahedral sites. It is proposed that most of the features in the 15,000–30,000 cm^{-1} region of these spectra are due to spin-forbidden transitions of Fe^{2+}.

The spectra of all minerals show a double-band system in the near infrared region due to spin-allowed transitions of octahedrally-bonded Fe^{2+}. The splitting of the bands is attributed to the dynamic Jahn-Teller mechanism.

A relatively intense polarized band at approximately 14,000 cm^{-1}, assigned to $Fe^{2+} \rightarrow Fe^{3+}$ interaction, occurs in the spectra of chlorite, biotite and some phlogopites. This band, together with polarized high-energy charge transfer processes, is the cause of pleochroism in sections of these minerals perpendicular to the (001) cleavage.

Some evidence is also given that suggests the possibility of $Fe^{2+} \rightarrow Al^{3+}$ and $Fe^{2+} \rightarrow Ti^{3+}$, Ti^{4+} electronic interactions.

Introduction

It is evident from a study of the pertinent literature that an explanation for the colour and pleochroism of many silicate minerals lies in understanding the roles of Fe^{2+} and Fe^{3+} bound mainly to oxygens in the crystal lattices. Although several recent works have been devoted to this end (Burns 1965, 1966; White & Keester 1966; Newnham & Farrell 1967; Faye 1968) clearly it is a field requiring further work.

From ligand or crystal-field theory it is well known that the colours of materials are due to electronic transitions between *d*-orbitals centred on transition metal ions and/or processes in which there is electron transfer from an anion to a cation or from a cation of low oxidation number to one of higher number.

Although all such processes are of significance in understanding the colours and pleochroism of silicate minerals, the *d-d* spectra are especially important because the analysis of such spectra often makes it possible not

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only to identify the absorbing cations but also to determine directly the approximate geometry of the sites in which they are located in the crystal lattice.

Such an approach has been used previously in interpreting the optical absorption spectra of the micas muscovite, lepidolite and fuchsite (Faye 1968). As a continuation of this kind of work, the present paper deals with the spectra of the sheet silicates chlorite, biotite and phlogopite, and of the naturally-occurring hydrous ferrous phosphate, vivianite.

The spectra of chlorite, biotite and phlogopite show spin-allowed *d-d* bands in the near infrared which are due to pseudo-octahedrally-coordinated Fe^{2+}. The visible spectra are very complex and are dominated, at least in the case of chlorite, by spin-forbidden *d-d* bands of six-coordinate Fe^{2+} and also probably Fe^{3+}. A relatively intense polarized band at approximately 14,000 cm^{-1} (719 mμ) occurs in the spectra of all these minerals and is partly responsible for the pleochroism of sections $\perp$ (001) in polarized light. This band is considered to be due to a photo-chemical oxidation-reduction process involving the interaction of Fe^{2+} and Fe^{3+}. However, this interpretation, at least for the spectrum of chlorite, differs from that of previous workers who considered the 14,000 cm^{-1} band to be due to a *d-d* transition of octahedrally-bonded Fe^{3+}. Polarized absorption in the ultraviolet also contributes to the pleochroism of transverse sections of the sheet silicates.

The spectrum of vivianite was examined in the present work because the visible portion of its spectrum was expected to display the features due to spin-forbidden transitions of octahedrally-coordinated Fe^{2+}.

Experimental

Mineral samples

The chlorite specimen was obtained from Mr. L. Moyd, curator of the display series of the National Mineral Collection, National Museum of Canada. Phlogopite No. 7 was obtained from Dr. J. Y. H. Rimsaite, Petrological Sciences Division, Geological Survey of Canada. The remaining mineral specimens were obtained from Mr. H. R. Steacy, curator of the reference series of the National Mineral Collection, Geological Survey of Canada. The locality of occurrence and partial analysis of these specimens are given in Table 1.

Determination of Fe^{2+} and Fe^{3+}

Sheet silicates. Total iron was determined by atomic absorption techniques. Fe^{2+} concentrations were determined titrimetrically (dichromate) after decomposition by a modification of the Cooke method (Hillebrand &

TABLE 1. CHEMICAL ANALYSES, COLOUR AND LOCALITY OF MINERALS

Minerals	Colour	Fe^{2+}		Fe^{3+}		Ti		Mn		Cr	
		%	M*	%	M*	%	M*	%	M*	%	M*
Vivianite Bingham, Utah	pale purple	33.5	16	<0.8	<0.4	—	—	—	—	—	—
Chlorite (Penninite) Blackstone Is., Parry Sound Dist. Ont.	green	5.2	2.8	0.6	0.3	0.04	0.015	0.02	0.01	0.04	0.02
Biotite Douglas Area, Ont.	dark brown-black	12.7	6.8	1.6	0.9	1.5	0.9	0.55	0.3	0.02	0.01
Phlogopite Templeton Twp., Que.	amber	1.1	0.5	0.2	0.1	0.3	0.2	—	—	—	—
Phlogopite N. Burgess, Ont.	medium brown	1.4	0.8	0.2	0.1	0.9	0.6	0.04	0.02	—	—
Phlogopite #7 Bancroft Area, Ont.	brown	4.4	2.3	0.4	0.2	0.4	0.25	0.08	0.04	—	—
Lepidolite Wakefield Twp., Que.	light brown	2.7	1.5	0.2	0.1	—	—	—	—	—	—

*M = concentration in moles/litre.

Lundell 1959) in which appropriate steps were taken to prevent atmospheric oxidation of Fe^{2+}. Fe^{3+} concentrations were determined by difference.

Table 1 gives the total concentrations of Ti, Mn and Cr. It is apparent that, with the possible exception of Ti^{3+} in the Templeton and N. Burgess phlogopite specimens, these elements in lower oxidation states would not seriously interfere analytically by being titrated as Fe^{2+}. The spectral evidence (i.e. band intensities) for the above phlogopites is consistent with the Fe^{2+} values given in Table 1, therefore there is no good reason for concluding that Ti^{3+} is present in these materials in sufficient concentration to give appreciably high Fe^{2+} results.

Vivianite. The determinations of Fe^{2+} and Fe^{3+} in vivianite were accomplished by conventional methods. It is to be noted however, that there was evidence for the oxidation of Fe^{2+} during the determination of Fe^{3+} (by thiocyanate) because no precautions were taken to prevent it. Therefore, the Fe^{3+} value given in Table 1 is to be considered a maximum.

Apparatus and experimental technique

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

Polarized spectra were obtained by mounting a rectangular sheet of "polaroid" film against the sample compartment wall containing the entrance ports for the sample and reference beams.

The basal sections of the sheet silicates were cleaved from "books" to give sheets of at least 2×2 mm that appeared to be uniform in colour and thickness.

Transverse sections cut approximately normal to the (001) cleavage plane of chlorite, phlogopite and biotite were obtained in the following manner: Compact "books" of each mineral were cut with a wire saw to give a flat face essentially perpendicular to the cleavage plane and having dimensions $\sim 3 \times 5$–10 mm. This face was mounted "end-on" in the centre of a mould of thermosetting epoxy resin ("Araldite"). The mould was then sawed into slices which were ground and polished in the usual manner to give sections $\sim$0.5–1 mm in thickness. Sufficiently-thin transverse sections of biotite could not be prepared that would allow the resolution of the σ-polarized spectrum (below).

For convenience it is assumed that the sheet silicates are uniaxial (e.g. $2V$ for the Douglas biotite $\sim 12°$), and that the σ-polarized spectrum (approximates the ω-spectrum) is observed when the electric vector and direction of propagation of the incident light are perpendicular to the optic axis. The spectrum observed when the electric vector is parallel to

the optic axis is called the π-polarized spectrum (approximate the ϵ-spectrum).

Sample thicknesses were measured with a micrometer.

Extinction coefficients (indicated on appropriate Figures) 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/litre and l is the thickness in cm. In estimating C it was assumed that the density of the sheet silicates is $\sim$3 g/ml and that of vivianite is 2.6 g/ml.

To facilitate the comparison of spectra and to follow the usual practice, "apparent" band or shoulder maxima are indicated by arrows in certain Figures. However, when the spectrograms are broken down into pseudo-gaussian peaks (by graphical methods), it is found than the real maxima for many features (especially those superimposed on relatively intense background absorption) are at lower energy than the "apparent" maxima. An extreme example of this is the 11,400 cm^{-1} band of spectrum A in Fig. 2, the maximum of which, on curve analysis, shifts to 11,900 cm^{-1}.

Net absorbance values for calculating approximate extinction coefficients 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.

Interpretation of Spectra

The absorption spectrum of vivianite

At the outset of the present work it was anticipated, on the basis of chemical analyses, that the absorption spectrum of the Blackstone Island

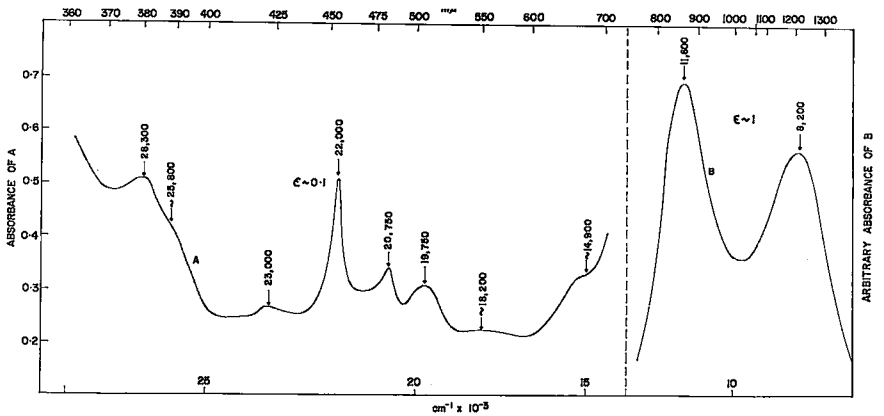

FIG. 1. Unpolarized spectra of (010) cleavage tablet of vivianite. A—thickness 0.14 cm; B—thickness, 0.035 cm.

chlorite might be dominated by features due to *d-d* transitions centred on Fe^{2+} rather than Fe^{3+} as in the previously studied micas (Faye 1968). Indeed, a preliminary examination of the complex spectrum of the chlorite (Fig. 2) suggested that the energy and intensity of the many bands and shoulders, especially in the 17,000–27,000 cm^{-1} region, could be explained more easily on the basis of spin-forbidden transitions of six-coordinate Fe^{2+} than on spin-forbidden transitions of six-coordinate Fe^{3+}. However, little is known of the former spectrum and, to the author's knowledge, no adequate assignment scheme has been made for the spin-forbidden transitions from the ${}^5T_{2g}({}^5D)$ ground state to states arising from terms of lower multiplicity of octahedrally-bonded Fe^{2+}. Therefore, for comparison purposes, a material was sought which contains Fe^{2+} in an octahedral array of six oxygens (OH^- or H_2O) as a principal constituent and which could be made to reveal a well-resolved absorption spectrum in

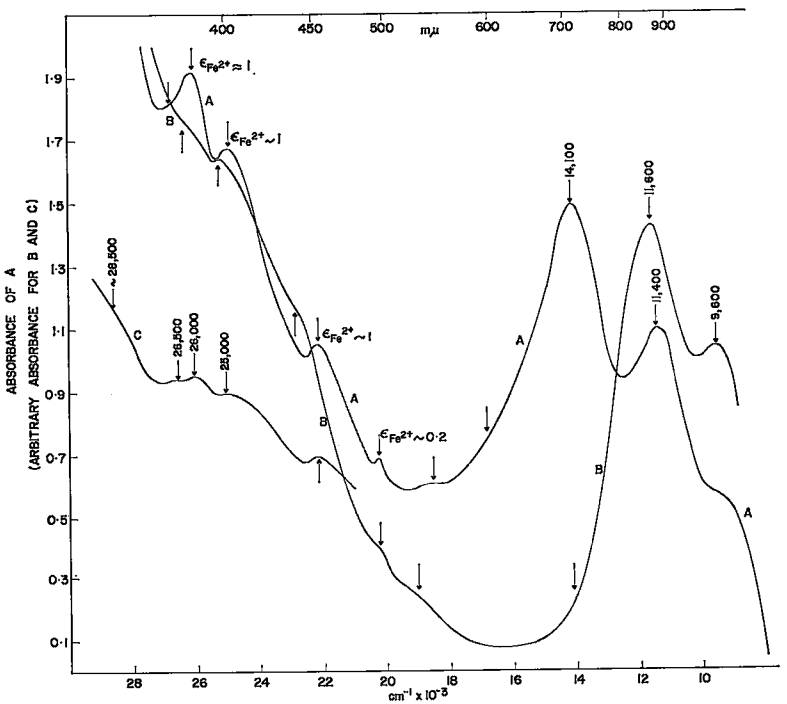

FIG. 2. Unpolarized spectra of Blackstone Island chlorite. A—basal section, thickness, 0.079 cm. B—transverse section, thickness, 0.12 cm. C—basal section, thickness, 0.033 cm.

NOTE:—The energy of most features of spectrum B are higher than corresponding features of spectrum A probably because the former are superimposed on more intense background absorption. On curve analysis the two spectra might possibly coincide.

the visible region, hopefully displaying features due to spin-forbidden transitions.

The mineral vivianite, $Fe_3(PO_4)_2.8H_2O$, was considered to fulfil these requirements ideally. The unpolarized absorption spectrum of a (010) cleavage tablet of this mineral is given in Figure 1.

Spin-allowed bands of octahedral Fe^{2+}. It is well established that the broad absorption envelope due to the spin-allowed transition $^5T_{2g}(^5D) \rightarrow {}^5E_g(^5D)$ is centred near 10,000 cm^{-1} in the spectrum of Fe^{2+} in an octahedral environment of oxygens (Low & Weger 1960; Cotton & Myers 1960; Burns 1965; Jones 1967). In the spectra of certain materials this absorption band may be split into two components separated by more than 3,000 cm^{-1} by the dynamic Jahn-Teller effect (Cotton & Myers 1960; Jones 1967). Such a splitting has been recently reported for the spectrum of Fe^{2+} in muscovite and lepidolite (Faye 1968).

It is known that Fe^{2+} lies in two kinds of six-coordinate sites in the lattice of vivianite (Mori & Ito 1950). In one site (A)Fe^{2+} is coordinated by four H_2O in a plane and by two trans-O^{2-} (from PO_4^{3-} units); in the other site (B) two H_2O are coordinated in a cis-arrangement and the remaining sites are occupied by O^{2-}.

Bond lengths and angles for the two coordination sites were calculated by using the structural data of Mori & Ito in a bond-and-angle-scan computer program (Gabe 1967), and the results are summarized in Table 2.

TABLE 2. BOND LENGTHS AND ANGLES OF Fe^{2+} SITES IN VIVIANITE

	Site A		Site B	
Bond lengths	1.97–2.00 Å	(6)	1.97–2.00 Å	(6)
Bond angles	88.9–81.1°	(10)	84.5–88.5	(6)
" "	84.7°	1	91.5–95.4	(6)
	95.5°	1		

From the above it is concluded that the two sites are sufficiently similar that the perturbing field around each kind of Fe^{2+} is nearly that of a regular octahedron. Therefore, it is reasonable to assume that the relatively widely separated bands at 11,600 and 8,200 cm^{-1} in spectrum B of vivianite in Fig. 1 are due to a lowering of the degeneracy of the upper ^5E_g state of octahedrally-bonded Fe^{2+} by the dynamic Jahn-Teller mechanism instead of being due to Fe^{2+} in two sites of different field strength. Indeed, if each of the two bands are those of Fe^{2+} in different sites it might be expected that each would show some splitting or fine structure due to low symmetry components and/or the Jahn-Teller mechanism.

By way of support for the above arguments it is worth noting that the

spectrum of the $Fe(OH_2)_6^{2+}$ unit in $Fe(NH_4)_2SO_4 \cdot 6H_2O$ (Tutton's salt) shows bands at 10,800 and 8,400 cm^{-1}. The splitting of these bands was thought by Cotton & Myers (1960) to be due to tetragonal and rhombic distortions of the $Fe(OH_2)_6^{2+}$ octahedron. However, Montgomery *et al.* (1967) have recently shown that the water molecules in $Fe(NH_4)_2SO_4 \cdot 6H_2O$ are arranged about the Fe^{2+} ion in an almost regular octahedron. Therefore, it is concluded that the band splitting of some 2,400 cm^{-1} in the spectrum of the Tutton's salt is a manifestation of the dynamic Jahn-Teller effect—an explanation in line with that of Cotton & Myers for the splitting of the absorption envelope in the spectra of other materials containing octahedrally-bonded Fe^{2+}.

The subject of the Jahn-Teller splitting in the spectra of the sheet silicates will be taken up again later in this paper.

Spin-forbidden bands of octahedral Fe^{2+}. From theoretical molecular spectroscopy, the well-known spin multiplicity role forbids changes in the net number of unpaired electrons in a "*d-d*" transition of an absorbing ion. However, the intensities of bands due to such a spin-forbidden transition are generally an order of magnitude less than those due to so-called spin-allowed transitions such as the $^5T_{2g} \rightarrow {}^5E_g$ transition of octahedrally-coordinated Fe^{2+} ($\epsilon \sim 1$ litre/mole-cm).

Partial energy-level diagrams are available showing the approximate manner in which the states arising from the triplet and singlet free-ion terms vary with the strength of the octahedral field (Cotton 1963; Burns 1965; Figgis & Lewis 1966), and it is evident from these that a relatively rich spin-forbidden spectrum, in the visible region, is to be expected. Many of the transitions are to triplet states (e.g. from ^3H), and some of these should be essentially field-independent judging from energy-level diagrams (e.g. Burns 1965).

Octahedrally-bonded Fe^{3+} also displays a complex and weak spin-forbidden absorption spectrum in the visible region (Ballhausen 1962); however, in the vivianite under study the molar ratio of $Fe^{2+}/Fe^{3+} > 40:1$; therefore it is reasonable to assume that all the bands and shoulders in the 15,300–30,000 cm^{-1} region of spectrum A of Fig. 1 are those due to spin-forbidden transitions of Fe^{2+}.

The spectra of vivianite in Figs. 1 and 3 appear to be better resolved and more detailed than those of certain other materials that show spin-forbidden features of octahedrally-coordinated Fe^{2+} (e.g. $FeSO_4$ in H_2SO_4 solution, Jorgensen 1954; $Fe(OH_2)_6^{2+}$ in various hosts, Jorgensen 1962; $FeCl_2.2H_2O$, Lawson (1966). The extinction coefficients of all the spin-forbidden bands appear to be ≤ 0.1 l/mole-cm; these are of the same order of magnitude as those reported by Jorgensen (1954). It is significant that $\epsilon \sim 0.1$ for the most intense feature, i.e. at 22,000 cm^{-1} is approximately one tenth that of the spin-allowed bands in the infrared region.

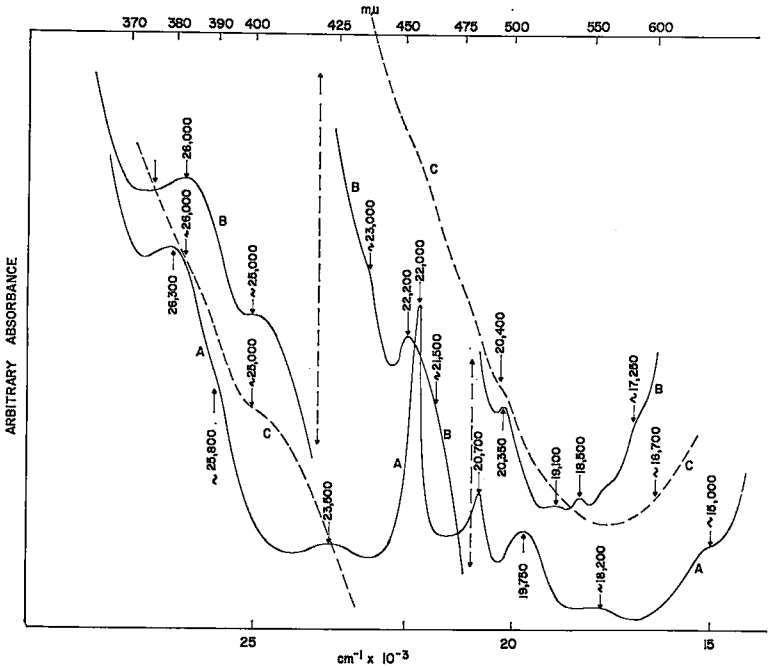

FIG. 3. Unpolarized spectra of vivianite, chlorite and biotite. A—vivianite, (010) cleavage tablet, thickness, 0.14 cm. B—chlorite, basal section, thickness, 0.10 cm. C—biotite, basal section, thickness, $\sim 5 \times 10^{-3}$ cm.

The sharpness of the bands at 22,000 and 20,750 cm^{-1} suggests that they are associated with transitions to essentially field-independent states (Dunn, 1960) and this observation may be of future value in making transition assignments.

Interpretation of the spectra of chlorite and biotite in the 15,000–30,000 cm^{-1} region

The spectra of the Blackstone Island chlorite and the Douglas biotite are shown in Figs. 2 and 3. The chlorite spectrum is resolved in much greater detail than that of biotite largely because it is affected by less intense background (charge-transfer) absorption. The complexity of the former suggests that if more than one absorbing cation (e.g. Fe^{2+} and Fe^{3+}) is present in the lattice and several coordination sites are possible, then an unequivocal interpretation of the spectrum would be difficult.

It is reasonably well established that Fe^{2+} is located in six-coordinate sites in both chlorite and biotite specifically, and in the trioctahedral and dioctahedral micas in general. It has been suggested that Fe^{3+} occurs in tetrahedral sites in a phlogopite (Steinfink 1962) and in a synthetic iron

mica (Donnay *et al.* 1964). On the other hand, absorption spectra have confirmed that Fe^{3+} occurs in octahedral sites in muscovite, lepidolite and fuchsite (Faye 1968) and it is assumed that it also occupies six-coordinate sites in the sheet silicates of the present work.

The six-coordinate sites of the "talc" and "brucite" layers of chlorite (Shirozu & Bailey 1965) and the "talc" layer of a synthetic biotite (Donnay *et al.* 1964) seem to be only moderately distorted from octahedral symmetry judging from the reported bond distances and angles. Therefore, the absorption spectra of the iron ions in such sites may not be appreciably complicated by features due to low-symmetry perturbations

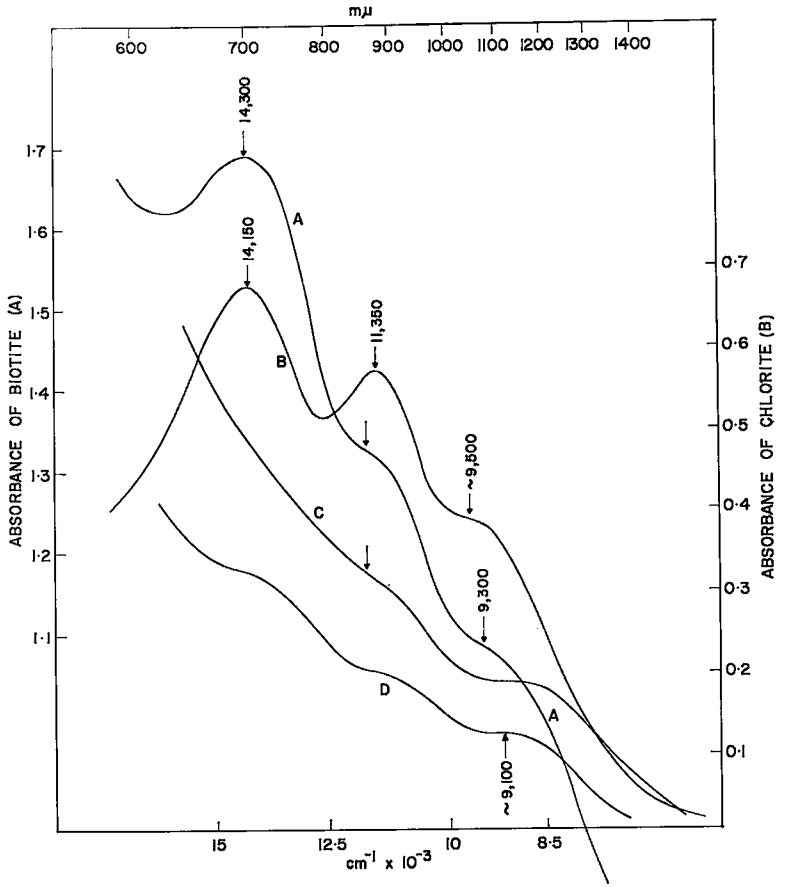

FIG. 4. Unpolarized spectra of basal sections of biotite, chlorite and phlogopites. A—biotite, thickness, $\sim 5 \times 10^{-3}$ cm. B—chlorite, thickness, 0.33 cm. C—phlogopite No. 7, thickness, 0.01 cm. D—phlogopite, N. Burgess, thickness 0.018 cm.

of the crystal field, especially if the field strength of the oxygens and hydroxyls are not much different.

The Fe^{2+}/Fe^{3+} ratio (Table 1) for both the chlorite and biotite samples is of the order of 10:1, therefore it is reasonable to expect that the spectra of these minerals would be dominated mainly by features attributable to pseudo-octahedrally-bonded Fe^{2+}, especially if the extinction coefficients for the two ions are of the same order of magnitude.

From Figs. 2 and 3 it is obvious that the spectra of chlorite and biotite are much more intense than that of vivianite in the 15,000–30,000 cm^{-1} region. Such intensity enhancement in silicate minerals is not uncommon. For example, the extinction coefficients of the more intense field-independent bands of Fe^{3+} in muscovite (Faye 1968) and epidote (unpublished work by the author) are approximately 1–2 l/mole-cm. The greater spectral intensities in the silicates, may be due in part to a greater tendency for vibronic interactions (i.e. mixing of electronic and vibrational states). Another probable factor is the stealing of intensity by *d-d* bands from underlying charge-transfer bands. (Such a mechanism is strongly suggested by the polarized spectra of chlorite in Fig. 5, to be discussed later.)

It is reasonable then, to argue that the spin-forbidden transitions of

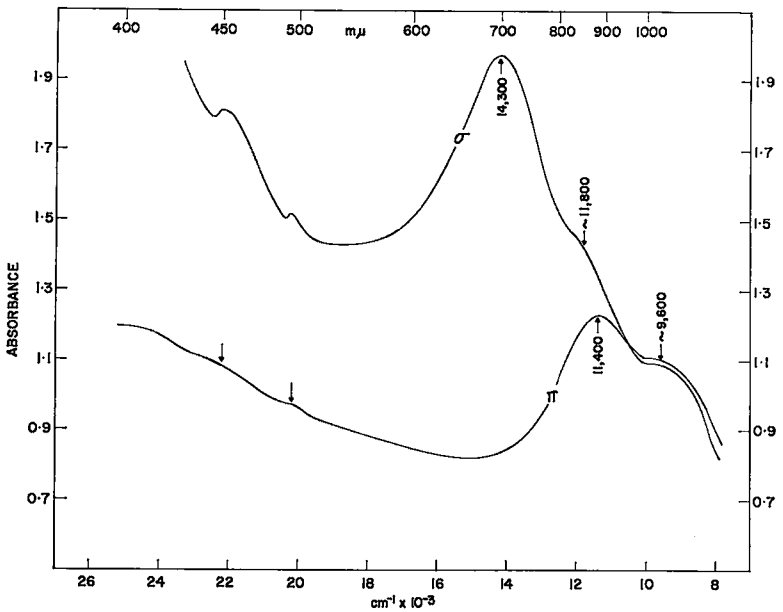

FIG. 5. σ- and π-Polarized absorption spectra of transverse section of chlorite, thickness 0.05 cm. Angle between positions giving σ- and π-spectra = 90° ± 2°.

Fe^{2+} in pseudo-octahedral sites of chlorite and biotite might gain intensity through similar mechanisms and that consequently the spectra of the minerals in the 15,000–30,000 cm^{-1} region are probably composed largely of bands due to this ion.

Tetrahedrally-bonded Fe^{2+}, as in diopside (White & Keester 1966) and in certain metal oxides (Bates, White & Roy 1966) has a single absorption band ($^5E \rightarrow {}^5T_2$) near 2μ. The spectra of all specimens of the present work were examined between 1.3 and 3μ and no bands were found that could be attributed to *d-d* transitions. Therefore, it can be concluded, as expected, that the sheet silicates do not contain appreciable amounts of Fe^{2+} in tetrahedral sites. It also follows that none of the features in the 15,000–30,000 cm^{-1} portion of the spectra can be assigned to spin-forbidden transitions of this ion.

Comparison of the spectra of vivianite, chlorite and biotite. For comparison purposes, the spectra of vivianite, chlorite and biotite are given in Fig. 3. It is apparent that a number of features of the chlorite spectrum especially, can be matched with those of vivianite to suggest that they are of common origin, i.e. due to spin-forbidden transitions of pseudo-octahedrally-bonded Fe^{2+}. The similarity of the spectra is emphasized by the following tabulation (Table 3) of peak and shoulder energies taken from Figs. 2 and 3.

TABLE 3. COMPARISON OF ENERGIES OF SPECTRAL BANDS OF VIVIANITE, CHLORITE AND BIOTITE

Vivianite cm^{-1}	Chlorite cm^{-1}	Biotite cm^{-1}
	28,500 perceptible	
	26,500 perceptible	
26,300 strong	26,000 strong	26,000 perceptible
25,800 perceptible	25,000 strong	25,000 strong
23,500 weak	23,500 weak	
22,000 strong	22,200 strong	22,000 perceptible
	21,500 doubtful	
20,700 sharp	20,350 sharp	20,400 pronounced
19,750 pronounced	19,100 weak	
18,200 weak	18,500 weak	
	17,250 perceptible	
		16,700 perceptible
15,000 perceptible		

Note: perceptible is used to denote a definite band or shoulder where relative intensity is in doubt.

The Fe^{3+} concentration of the chlorite specimen is appreciable ($\sim$0.3 *M*) and there seems to be spectral evidence for its presence in six-coordinate sites. Muscovite, for example, has octahedral sites that are probably not too different from those of the "talc" layer of chlorite. The spectrum of Fe^{3+} in muscovite has been reported in previous work (Faye

1968) and the relatively intense band ($\epsilon \sim 2$ l/mole-cm) due to the field-independent ${}^6A({}^6S) \rightarrow {}^4A\,{}^4E({}^4E)$ transition occurs at 22,600 cm^{-1}, and the bands due to transitions to the ${}^4T(D)$ and ${}^4E(D)$ states have maxima at 26,600 and 27,400 cm^{-1} respectively. The corresponding transitions for Fe^{3+} in chlorite may well occur at ~21,500 (spectrum B, Figure 3) 26,500 and 28,500 cm^{-1} (spectrum C, Figure 2). The broadening of the 22,200 cm^{-1} band on the low-energy side, especially in the former spectrum strongly suggests an unresolved component at approximately 21,500 cm^{-1}.

The extinction coefficients calculated on the basis of the Fe^{2+} concentrations of chlorite are ~0.2 l/mole-cm for the 20,200 cm^{-1} band and ~1 l/mole-cm for each of the 22,200, 25,000 and 26,000 cm^{-1} bands of spectrum B in Figure 2. If Fe^{3+} concentrations are used in such calculations the extinction coefficients are an order of magnitude larger than the above, and there is no obvious reason why spin-forbidden transitions of Fe^{3+} should be so enhanced relative to spin-forbidden transitions of Fe^{2+}.

White & Keester (1966) examined the unpolarized spectrum of a basal section of a chlorite and, although it was highly compressed in reproduction, it appears to be essentially the same as the spectra of Figs. 2 and 3 (except that White & Keester did not record any high-energy charge-transfer absorption). The total iron concentration of their chlorite was expressed as Fe_2O_3 and they apparently assumed that the Fe^{2+} concentration was negligible, for they assigned all the spectral features in the 15,000–30,000 cm^{-1} region to Fe^{3+}. As we will see later, certain other of their assignments are not in accord with those of this paper.

Although the spectra of biotite in general are poorly resolved in the visible region because of intense background absorption, several features appear in Spectrum C of Fig 3 that correlate well with certain of those of the chlorite spectra (Table 3) and therefore it is reasonable to conclude that these are due to six-coordinate Fe^{2+} in biotite.

Because of the similarity of the biotite and chlorite spectra (also in the near infrared region as we will see later) it is probable that Fe^{2+} is accommodated in similar sites in the two minerals.

Either these must be the sites of the "talc" layer, since these are the only ones in the biotite structure, or, the sites in the "talc" and "brucite" layers of chlorite produce essentially the same crystal fields around the Fe^{2+} ion.

It is of interest to note that Shirozu & Bailey (1965) concluded that 60% of the Fe^{2+} was concentrated in the talc sheet of a high-iron (28% Fe^{2+}) chlorite. Because Fe^{2+} seems to favor the talc sites, it is possible that in chlorites of lower Fe^{2+} concentration, such as the present specimen, the proportion of this ion in the talc sites may be considerably higher.

The polarized spectra of transverse sections of chlorite, phlogopite and biotite

The unpolarized spectra of basal sections of chlorite and biotite in Figs. 2 and 4, and the σ-polarized spectra of transverse sections of chlorite and phlogopite in Figs. 5 and 6 respectively, each show a relatively intense absorption band or shoulder with a maximum at approximately 14,000 cm^{-1}. However, this feature is of low intensity in the unpolarized spectra of transverse sections of chlorite (Figs. 2, 7), biotite (Fig. 7) and

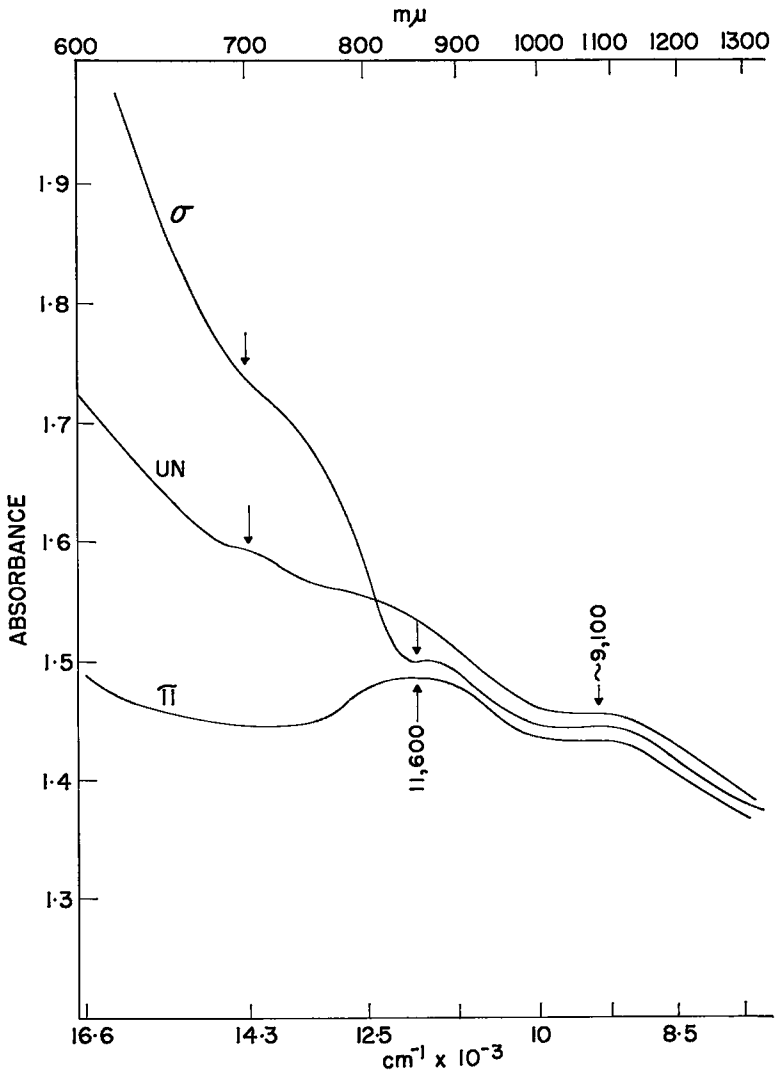

FIG. 6. σ- and π-Polarized and unpolarized (UN) spectra of transverse section of Templeton phlogopite, thickness, 0.056 cm.

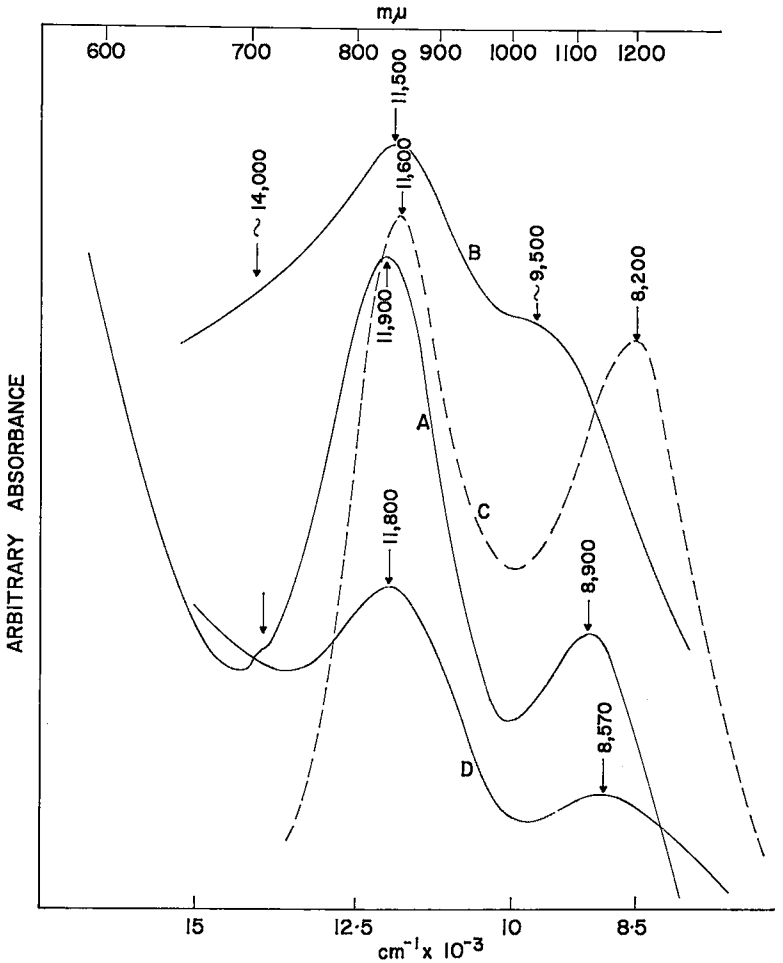

FIG. 7. Unpolarized spectra of biotite, chlorite, vivianite and lepidolite. A—biotite, transverse section, thickness, $\sim 3 \times 10^{-3}$ cm. B—chlorite, transverse section, thickness, 0.05 cm. C—vivianite, (010) cleavage tablet, thickness, 0.14 cm. D—lepidolite, basal section, thickness, 0.071 cm.

phlogopite (Fig. 6) and is missing from the π-polarized spectra (Figs. 5, 6).

All of the above-mentioned spectra exhibit two bands in the 11,000–8,000 cm^{-1} region that are similar to those of the spectra of vivianite and lepidolite (Fig. 7). Because these bands are not polarized in the manner of the 14,000 cm^{-1} band it is concluded that they are due to pseudo-octahedrally-bonded Fe^{2+} and that their splitting is of the same origin as that in the spectra of vivianite and lepidolite (Faye 1968), i.e. due to the dynamic Jahn-Teller mechanism.

The polarization of the 14,000 cm^{-1} band and proposed $Fe^{2+} \rightarrow Fe^{3+}$

interaction. Because the intensity of the 14,000 cm^{-1} band varies from maximum to minimum in the σ- and π-polarized spectra respectively, of transverse sections of the sheet silicates, it is evident that light is preferentially absorbed when the vibration direction or electric vector of the incident light lies in the "infinite" planes of octahedrally-coordinated cations.

Figure 8 is a highly diagrammatic representation of certain atoms (ions) of the talc layer of chlorite, phlogopite or biotite projected on the (010) plane. From this it can be seen that two lobes of the d_{xy} orbital of the t_{2g} set of 3*d*-orbitals of iron ions, for example, lie in the plane (001) of octahedrally-bonded cations.

It is apparent that these orbital lobes project between the negatively charged "ligands" and that there is possible overlap of d_{xy} orbital lobes of adjacent cations. Such orbital overlap can occur in the (001) plane also with respect to two lobes of each of the d_{xz} and d_{yz} orbitals. Thus, as a maximum, six of the 12 lobes of the t_{2g} set of orbitals can participate in orbital overlap with neighboring cations. The remaining six lobes of the t_{2g} set of orbitals do not lie in the (001) plane and therefore cannot participate in "metal-metal" bonding. The same is of course true of the e_g orbitals which are directed at the oxygens and hydroxyls.

In π-polarized light the electric vector of the radiation field does not interact appreciably with the overlapping d_{xy} orbital lobes and the 14,000 cm^{-1} band is not detectable. In the unpolarized spectra of transverse sections the band appears weakly, probably because of the low intensity of the electric field component in the σ-polarized plane in the beams of unpolarized light entering the cell-compartment of the spectrophotometer.

The ~14,000 cm^{-1} band is attributed to $Fe^{2+} \rightarrow Fe^{3+}$ electronic interaction rather than to $Fe^{2+} \rightarrow Al^{3+}$, for example, because the difference between the donor energy-level of Fe^{2+} and the energy-level of the acceptor ion is probably much more than 14,000 cm^{-1} for the latter process. Interaction of the $Fe^{2+} \rightarrow Al^{3+}$ kind in orthopyroxenes has been proposed by Burns (1965) and is considered to result in absorption of energy in the ultra-violet region of the spectrum. Indeed, as we will see below (Fig. 9) there is also evidence for such interaction in the sheet silicates.

In general, the extinction coefficients for charge-transfer processes are found to be ~10^3 l/mole-cm or higher. However, ϵ for the 14,200 cm^{-1} peak in the σ-spectrum of chlorite in Figure 5, for example, is ~5 l/mole-cm based on total iron concentration, and this value is of the same order of magnitude as those for the spin-allowed *d-d* transitions of octahedrally-bonded Fe^{2+}. The low intensity here however, is probably because the system is very "dilute" with respect to interacting species.

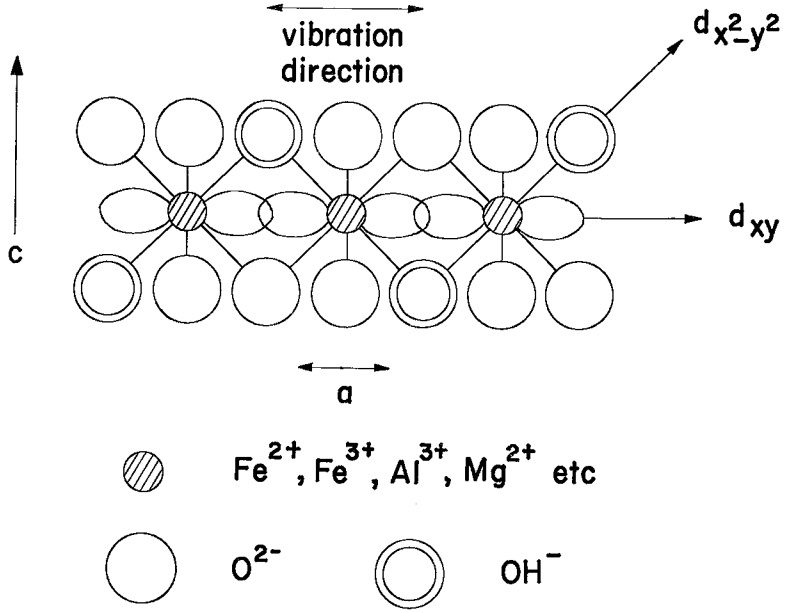

FIG. 8. Diagrammatic representation, on the (010) plane, of atoms of talc sheet of chlorite, phlogopite or biotite showing overlapping *d*-orbitals. Molecular axes indicating orientation of *d*-orbital lobes arbitrarily chosen and not related to crystallographic axes.

If the foregoing explanation of the origin of the ~14,000 cm^{-1} band is correct, it is reasonable to suggest that its intensity would be a function of both the concentration of total iron and the ratio of Fe^{2+}/Fe^{3+}, i.e. on the probability of Fe^{2+} and Fe^{3+} being close enough to interact, either directly on each other, or through several neighboring cations. Indeed, evidence for such rough correlations is inherent in Table 1 and in the unpolarized spectra of basal sections of chlorite, biotite and phlogopites in Figs. 4 and 6 and the lepidolite in Figure 7 and is summarized in Table 4.

TABLE 4. CORRELATION OF INTENSITY OF ~14,000 cm^{-1} BAND WITH TOTAL Fe AND Fe^{2+}/Fe^{3+}

Mineral	Relative Intensity of 14,000 cm^{-1} band	Total Fe (moles/litre)	~Fe^{2+}/Fe^{3+}
Chlorite	strong	3.1	9
Biotite	strong	7.7	8
Phlogopite, N. Burgess	moderate	0.9	8
Phlogopite, Templeton	weak	0.6	5
Phlogopite, No. 7	nil	2.5	11
Lepidolite	nil	1.6	15

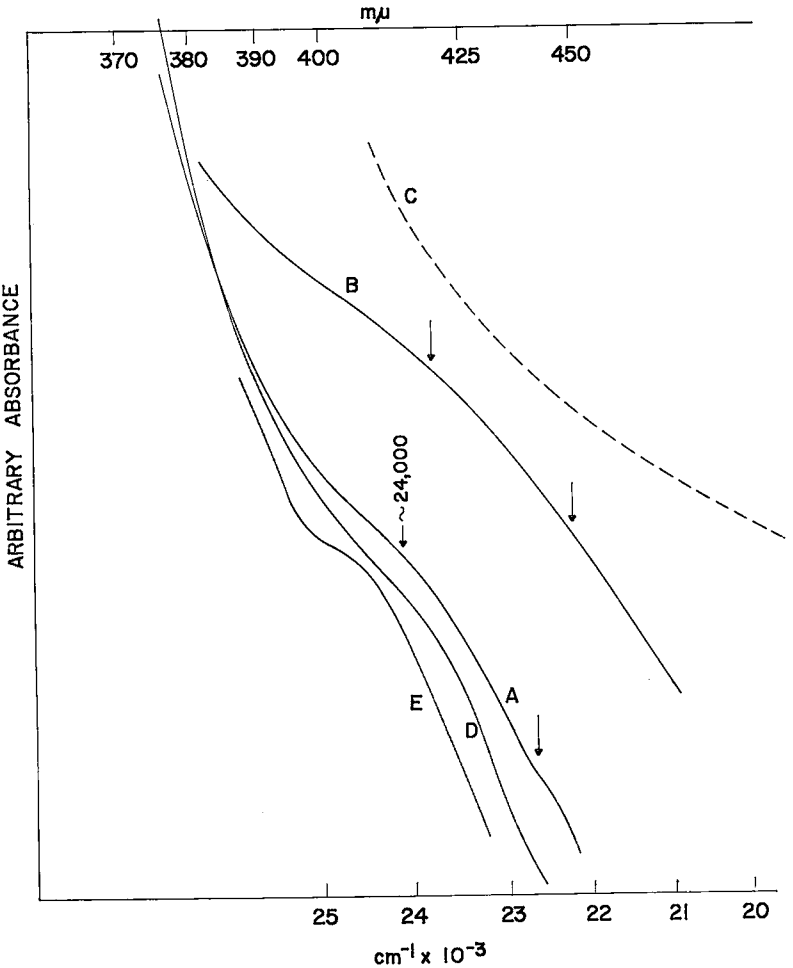

FIG. 9. Unpolarized spectra of biotite and phlogopites. A—phlogopite No. 7, basal section, thickness, $\sim 5 \times 10^{-3}$ cm. B—phlogopite, Templeton, basal section, thickness 0.015 cm. C—phlogopite, Templeton, transverse section, thickness 0.086 cm. D—phlogopite, N. Burgess, basal section, thickness, 0.018 cm. E—biotite, basal section, thickness $\sim 5 \times 10^{-3}$ cm.

The data in Table 4 suggest that the $\sim$14,000 cm^{-1} band might not be observed in the spectrum of a trioctahedral mica or chlorite unless the total Fe concentration is $\gtrsim 0.5\ M$ and the Fe^{2+}/Fe^{3+} ratio is $< \sim 10{:}1$. The approximate lower limit of the Fe^{2+}/Fe^{3+} ratio cannot be determined from the present work.

White & Keester (1966) assigned the strong 14,280 cm^{-1} band in their unpolarized spectrum of a basal section of chlorite to the ${}^6A_{1g} \rightarrow {}^4T_{2g}{}^4(G)$

transition of octahedrally-coordinated Fe^{3+}. In view of the present work this assignment seems to be incorrect, again probably because they assumed that the Fe^{2+} concentration of their specimen was trivial.

Evidence for $Fe^{2+} \rightarrow Ti^{3+}$, Ti^{4+} interaction in phlogopites and biotite. The 25,000 cm^{-1} shoulder in the biotite spectra (C and E in Figs. 3 and 9 respectively) is very pronounced and is broadened on the low energy side in much the same manner as the shoulders in the 23,000–25,000 cm^{-1} region of the phlogopite spectra in Fig. 9. Table 1 shows that the titanium concentration of the biotite and phlogopites is appreciable (0.2 to 1.2 *M*) and it is proposed, therefore, that the shoulders may be due to the electronic interaction of Fe^{2+} and Ti^{3+} and/or Ti^{4+} interaction. Support for this proposition is given by spectrum C, Fig. 9 of a transverse section of the Templeton phlogopite. This spectrum does not show the broad shoulder at ~24,000 cm^{-1} and in this regard is similar to the unpolarized spectrum (B, Fig. 2) of the transverse section of chlorite in which the 14,000 cm^{-1} band due to the $Fe^{2+} \rightarrow Fe^{3+}$ interaction is barely discernible.

It is unlikely that the shoulder under discussion could be due to the $^2T_{2g} \rightarrow {}^2E_g(D)$ transition of octahedrally-coordinated Ti^{3+}. This transition is known to occur at approximately 20,000 cm^{-1} in $Ti(OH_2)_6^{3+}$ (Ilse & Hartmann 1951) and $AlCl_3 . 6H_2O$ (Walker & Carlin 1967) and there is no good reason to expect that the crystal field strength would be ~4,000 cm^{-1} higher in the trioctahedral micas.

All the phlogopite spectra of the present work are poorly resolved in the visible region and it is probable that the fine structure that is evident in the chlorite spectrum is swamped by the combination of high-energy charge-transfer absorption and the process giving rise to the 24,000 cm^{-1} shoulder.

Ultraviolet charge-transfer absorption in chlorite and phlogopite: $Fe^{2+} \rightarrow Al^{3+}$ interaction. Figure 10 shows the near-ultraviolet spectra of very thin basal sections of the chlorite (A) and the Templeton phlogopite (B). Each spectrum contains a maximum, which because of its intensity ($\epsilon \sim$ 100–200 l/mole-cm, based on total Fe), cannot be assigned to *d-d* transitions. Because sufficiently thin transverse sections of the two minerals could not be prepared it was not possible to determine the polarizability of the 39,000 and 37,000 cm^{-1} features in spectra A and B respectively. It is tempting to suggest that these bands (shoulders) may be due to the $Fe^{2+} \rightarrow Al^{3+}$ charge-transfer process discussed previously. As such they should be polarized in a similar manner to the 14,000 cm^{-1} band, and their low-energy limbs should be seen to rise and fall in the visible region as does the background absorption in the polarized spectra of Figs. 5 and 6.

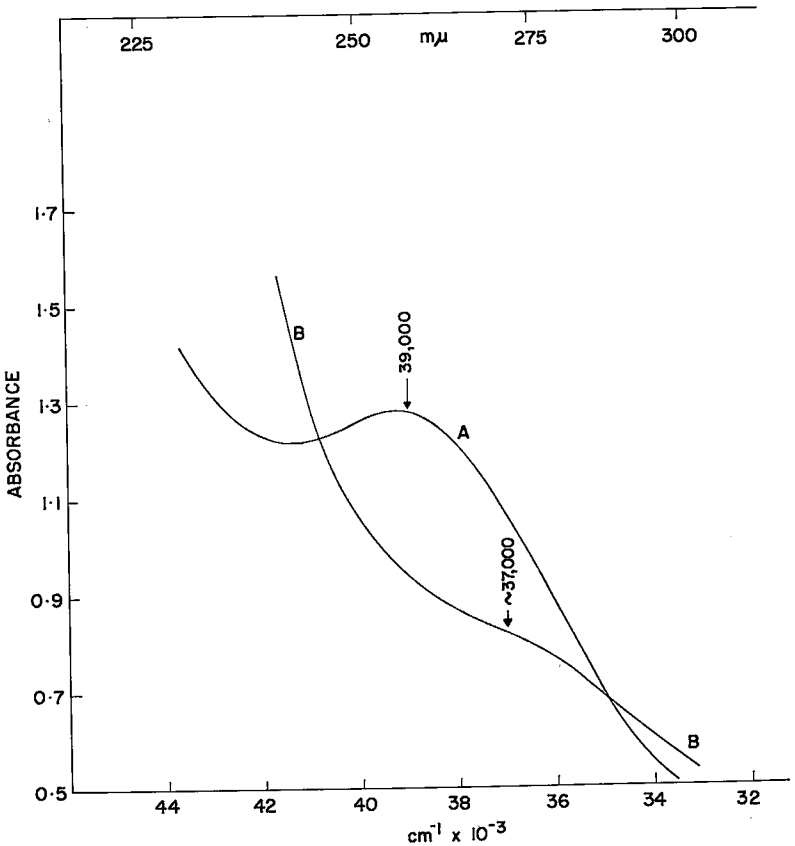

FIG. 10. U.V. spectra of basal sections of chlorite and Templeton phlogopite. A—chlorite, thickness $\sim 2 \times 10^{-3}$ cm. B—phlogopite (Templeton) thickness $\sim 1 \times 10^{-3}$ cm.

It is possible that the intense high-energy charge-transfer absorption on which the 39,000 and 37,000 cm^{-1} features are superimposed also contributes to the background absorption in the visible region and this may or may not be polarized in the manner of the $\sim$14,000 cm^{-1} band.

Intensity-stealing. It is of interest to note the intensities of the 22,200 and 20,200 cm^{-1} peaks in the σ- and π-spectra of chlorite in Fig. 5. The original spectrogram (in which features are more pronounced) indicates that the bands in the visible region are not polarized themselves, but that their intensities are directly related to that of the underlying charge-transfer absorption which is polarized. Such intensity-stealing has been considered recently in a theoretical way by Fenske (1967).

Pleochroism of transverse sections of chlorite, biotite and phlogopite

From the foregoing it is possible to offer a facile explanation for the

relatively intense visible ($\sim$14,000–25,000 cm^{-1}) pleochroism of transverse sections of chlorite, biotite and phlogopite.

Table 5 lists the colours of transverse sections of the minerals as they appear at "arms-length" in unpolarized $\sigma(\sim\omega)$ and $\pi(\sim\epsilon)$-polarized light. These can be easily correlated with the appropriate absorption spectra.

From the π-polarized spectrum in Fig. 5 it is obvious that there is little or no absorption of red light by the high-energy wing of the 11,400 cm^{-1} band of Fe^{2+}. Therefore, the yellow-green colour of the section is due primarily to the absorption of violet light by the higher-lying charge-transfer processes. In other words, the π-spectrum is little influenced by *d-d* transitions of either Fe^{2+} or Fe^{3+}.

TABLE 5. COLOUR OF TRANSVERSE SECTIONS IN UNPOLARIZED AND POLARIZED LIGHT

Mineral	Thickness cm	Unpolarized	σ-Polarized	π-Polarized
Chlorite	0.05	light green	blue-green to blue	to yellow-green
Phlogopite (Templeton)	0.056	light brown	dark red-brown	light yellow-brown
Biotite	0.03	brown	black	brown
	0.01	green-brown		light-green-brown

On the other hand, the blue-green colour of chlorite in σ-polarized light is due to the absorption of red light by the $Fe^{2+} \rightarrow Fe^{3+}$ band centred at 14,300 cm^{-1} and of violet light, again primarily by charge-transfer processes.

It is to be noted that White & Keester attributed the green colour of chlorite to ferric-iron—an interpretation not in accord with the present work.

Although the phlogopite spectra of Fig. 6 were not measured at energies higher than $\sim$17,000 cm^{-1}, it can be seen that charge-transfer absorption dominates the visible region. In all cases the brown colour is due to transmission of yellow, orange and red light. Although the intensity of the $Fe^{2+} \rightarrow Fe^{3+}$ band at 14,300 cm^{-1} is at a maximum in the σ-spectrum, the background absorption is so intense that relatively more red light is transmitted than in the π—or unpolarized spectra and the colour of the section is dark red-brown.

The pleochroism of biotite can be explained in a similar manner to that for the other two minerals. It is obvious of course, that no light is transmitted by the section in σ-polarized light and the material appears black. In relatively thin sections (transverse or basal) the low-lying wing of the charge-transfer band "retreats" to higher energy, thus exposing (or permitting the resolution of) the $Fe^{2+} \rightarrow Fe^{3+}$ band at 14,300 cm^{-1} and

also the shallow trough with a minimum near 16,000 cm^{-1} (see spectrum A, Fig. 4). The latter can be regarded as a "window" permitting the transmission of green-blue light and hence the green-brown colour of the mineral.

Acknowledgements

The author wishes to thank Drs. E. H. Nickel, P. G. Manning and W. Petruk for helpful discussions. Thanks are also due to Dr. E. J. Gabe for the bond-and-angle data for vivianite, to Mr. J. C. Hole and Miss E. Mark for the chemical analyses and to Mr. A. E. Harrington for the preparation of mineral sections.

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Manuscript received October 26, 1967