THE EFFECT OF CHARGE-TRANSFER PROCESSES ON THE COLOUR AND PLEOCHROISM OF AMPHIBOLES

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ABSTRACT

A study is reported of the polarized optical absorption spectra of the amphiboles riebeckite, crossite, glaucophane, holmquistite, hornblende, barkevikite and ferrohastingsite. The colour and pleochroism of the amphiboles are primarily the result of the polarization properties of electronic transitions associated with $Fe^{2+} \rightarrow Fe^{3+}$ and $O^{2-} \rightarrow Fe^{3+}$ charge-transfer processes. The former process is an important feature of the spectra of all the amphiboles; however, the latter is more important for calcic amphiboles. It is shown how the charge-transfer processes are thought to be related to the amphibole structure and to cation distribution.

The *a–c* sections of most of the monoclinic amphiboles examined show anomalous extinction, which is attributed to the non-coincidence of the principal vibration and absorption directions.

INTRODUCTION

It is well established that the colour and pleochroism of many silicate (and other) minerals is strongly influenced by the charge-transfer process between adjacent Fe^{2+} and Fe^{3+} ions, usually in structures where these ions share octahedral edges and there is possible overlap of t_{2g} orbitals (for example, see: Hush 1967; Faye 1968; and Faye *et al.* 1968). Specifically, this process has been invoked to explain, in part, the pleochroism of the alkali amphiboles, crocidolite (Littler & Williams 1965); riebeckite (Manning & Nickel 1969), and glaucophane (Bancroft & Burns 1969). However, the present work indicates that a somewhat more detailed study is required to explain adequately how the $Fe^{2+} \rightarrow Fe^{3+}$ interaction, together with other charge-transfer processes, influences the pleochroism of sodic and calcic amphiboles.

THE STRUCTURE OF AMPHIBOLES

The basic structure of monoclinic amphiboles is shown in Fig. 1 and certain details are presented in Figs. 2 and 7. Bond distances given in the latter figures are those determined by Papike & Clark (1968) and, for our needs, are considered to be representative of the amphiboles of this work.

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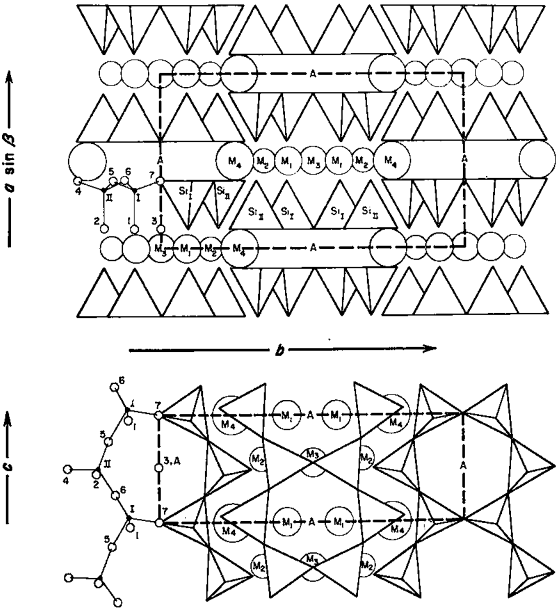


FIG. 1. Schematic (001) and (100) projections of the monoclinic amphibole crystal structure after Ernst (1968).

In this work we are principally interested in the strips of cations that parallel the *c*-axis and are sandwiched between inward-pointing bands of silica (alumina) tetrahedra. In the strips there are three non-equivalent six-coordinate sites, M_1, M_2, M_3, and one site, M_4, of six-to-eight-fold coordination (in this work we will assume eight-fold coordination).

Cations on M_1 and M_3 are each coordinated to four oxygens and two hydroxyls (cis for M_1, trans for M_3), and the cation on M_2 is coordinated to six oxygens. Cations on M_4 are coordinated only to oxygens. There are two of each of the M_1, M_2 and M_4 sites for every M_3 site in the unit cell.

EXPERIMENTAL DETAILS

Sample preparation

For those samples consisting of sufficiently large crystals (riebeckite, hornblende, ferrohastingsite and barkevikite), oriented sections containing the crystallographic axes were cut from the crystals with a wire saw, using the 110 prismatic cleavages as a guide. The crystals of holmquistite, glaucophane and crossite were too small for this procedure, and were embedded directly in a plastic mounting medium on glass slides. The

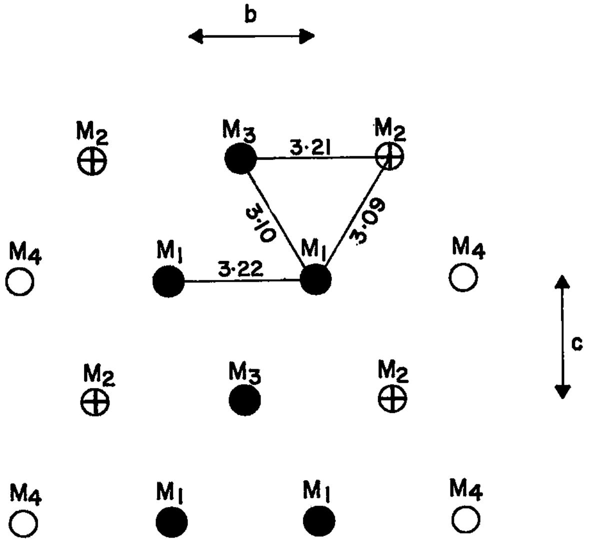


FIG. 2. Arrangement of cations and approximate distribution of iron ions in monoclinic alkali amphiboles. *M–M* distances are for glaucophane (Papike & Clark 1968).
● (M_1 and M_3)—sites favoured by Fe^{2+}
⊕ (M_2) —site favoured by Fe^{3+}
○ (M_4) —site favoured by alkali metal ions.

sections were ground down to the appropriate thickness for optical absorption measurements and polished. The crystallographic orientation was confirmed in each case by conoscopic optical interference figures.

The thickness of the mineral sections was estimated by the Duc de Chaulnes' method, *i.e.*, by using the fine focusing adjustment on the microscope.

The specimens of riebeckite, barkevikite, hornblende, and ferrohastingsite were obtained through the courtesy of Mr. L. Moyd, and the specimens of glaucophane, crossite and holmquistite were obtained through the courtesy of Mr. H. R. Steacy. Messrs. Moyd and Steacy are, respectively, curators of the display series of the National Mineral Collection, National Museum of Canada, and the reference series of the National Mineral Collection, Geological Survey of Canada.

Measurement of spectra

All spectra were measured at room temperature with a Cary-14 recording spectrophotometer. The standard sample compartment was replaced by a special housing which permitted the mounting of a Unitron

MPS petrographic microscope in each of the sample and reference beams (in either the infrared or visible mode) in a manner similar to that of Burns (1966). The mineral specimen, mounted on the stage of the sample-beam microscope, was oriented in the polarized light beam so as to measure the desired spectrum (*i.e.*, parallel to a given crystallographic direction). Glan prisms were used in lieu of the polarizers supplied with the microscopes. The spectra in Figs. 3, 6 and 8 were re-plotted on a linear energy scale before curve analysis.

SPECTRA OF AMPHIBOLES

Figs. 3, 4, 5, 6 and 8 show the polarized absorption spectra of *a-c* and *b-c* sections of a number of amphiboles, the partial analyses of which are given in Table 1. Except for minor shoulders in the 8,000–12,000 cm^{-1} range, (which we can assume to be due to internal transitions within six-coordinate Fe^{2+}) the $E//b$ and $E//c$ spectra are dominated by an asymmetric absorption envelope having a maximum between 15,000 and 17,000 cm^{-1}. $E//a$ (or a') spectra (*e.g.* see Fig. 4) are essentially featureless, showing a gentle increase in absorption in the visible region and finally rising sharply in the near UV region. The polarization properties of the absorption envelope in the visible region of the $E//b$ and $E//c$ spectra are primarily responsible for the dramatic visible pleochroism of the alkali amphiboles selected for this study. From previous work, cited above, it can be taken, with a fair degree of certainty, that this envelope represents the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process and that its intensity depends, in part, on the total iron concentration, the Fe^{2+}/Fe^{3+} ratio of the specimen and the distribution of iron among the available sites.

Figs, 3, 6 and 8 show that the principal band can be resolved into two components separated by approximately 3,000–4,000 cm^{-1}. In most cases the area under the low-energy component of $E//c$ spectra is approximately twice that under the high-energy component; for the $E//b$ spectra, the upper component is of comparable intensity (area) to the lower. The intensities of the two features in the holmquistite spectra are similar for both $E//c$ and $E//b$.

An important aspect of the present study is the observation that the direction (of the electric vector E) giving maximum intensity of the principal absorption band in the spectra of *a-c* sections of riebeckite, ferrohastingsite, barkevikite and hornblende, (*e.g.* Figs. 4 and 5) is not coincident with the crystallographic *c* axis and varies from specimen to specimen. The reasons for this are discussed in a subsequent section below.

A second important observation is that the UV-centered charge-transfer absorbance is relatively more intense in the spectra of the calcic amphiboles than in those of riebeckite, holmquistite and other sodic amphiboles. This is most evident when comparing the position of the minima of the spectra in Figs. 3–6 with those of Fig. 8. Figure 8, which is typical of the calcic amphiboles, also shows that the background absorbance is more intense in the *E*//*b* spectra than in *E*//*c*.

The spectra of riebeckite shown in Figs. 4 and 5 must be described in somewhat more detail for, as we will see, an understanding of these is important in interpreting the spectra of other amphiboles.

One rather remarkable visual effect exhibited by *a-c* sections of riebeckite is that the colour seems to undergo a change from blue-grey to bright blue as the section is thinned down. The spectra in Fig. 4 are those

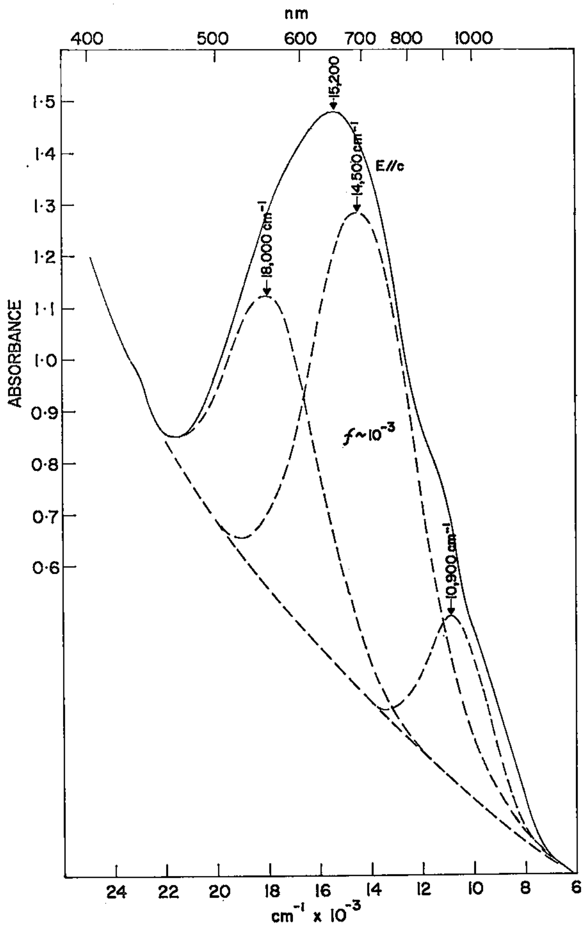


Fig. 3a

of a thin (~0.002–~0.003 cm) blue area of the Colorado riebeckite. It is evident that, as the angle between the electric vector (*E*) of polarized light and the *c*-axis is varied from 0° to 10°, there is a gradual and modest increase in intensity of both the UV-centered background absorption and the main, two-component $Fe^{2+} \rightarrow Fe^{3+}$ band in the visible region. At angles between 10° and 90° the intensity of the spectra decreases until a minimum is reached when $E \perp c$. Between 90° and 150° the intensity of the spectral features increases again until a maximum is reached at 190° when the spectrum is identical to that at 10°.

Figure 5 shows the spectral changes occurring when the orientation of a relatively thick (~0.004–~0.005 cm) blue-grey area of the same *a-c* section of riebeckite is varied in polarized light. Here again, the intensity of both the UV background absorption and the main band in the visible

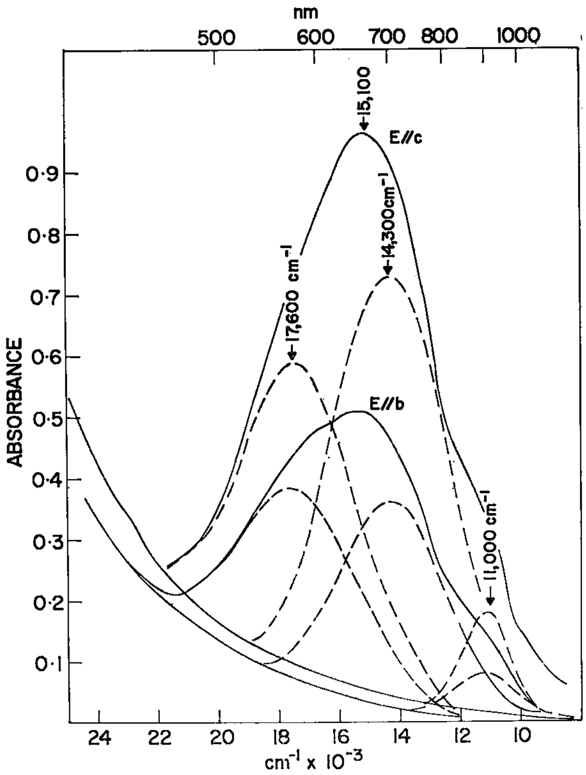


Fig. 3b

Figs. 3a and 3b: *E*//*c* and *E*//*b* spectra, respectively, of *a-c* and *b-c* sections of riebeckite; thickness of sections ~.001–~.002 cm.

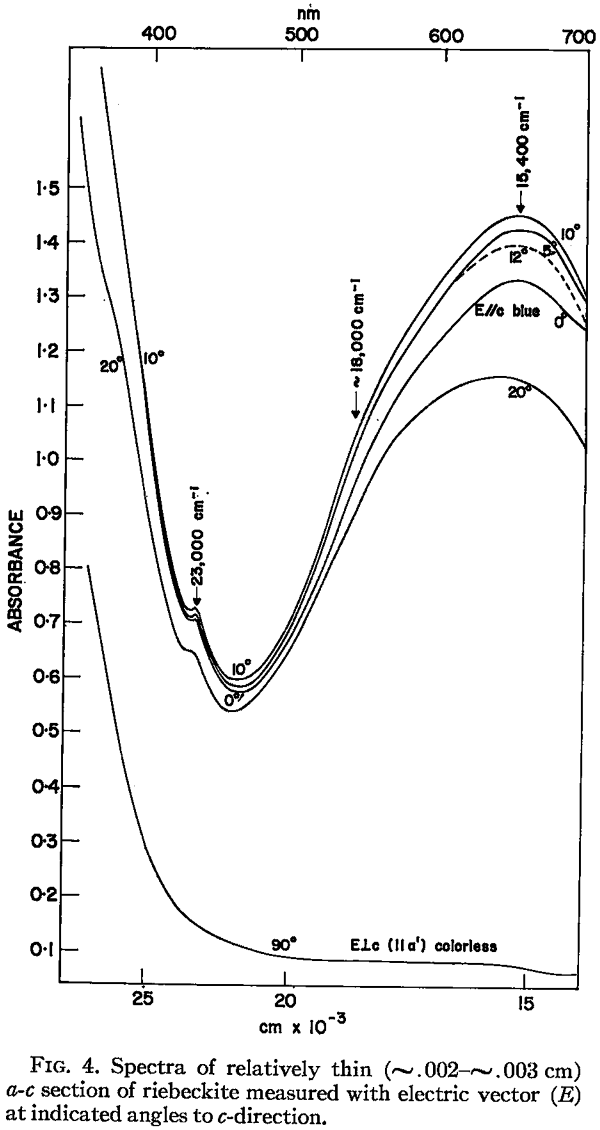


FIG. 4. Spectra of relatively thin (~.002–~.003 cm) *a-c* section of riebeckite measured with electric vector (*E*) at indicated angles to *c*-direction.

region rise and fall in concert; however, subtle and unequal rates of change of the intensity of the components at 18,000 cm^{-1} and 14,500 cm^{-1} result in a rather wide display of colours, as indicated in Fig. 5.

The visible polarized spectra of both *a-c* and *b-c* sections of specimens of the sodic amphiboles—glaucophane and crossite—were also recorded,

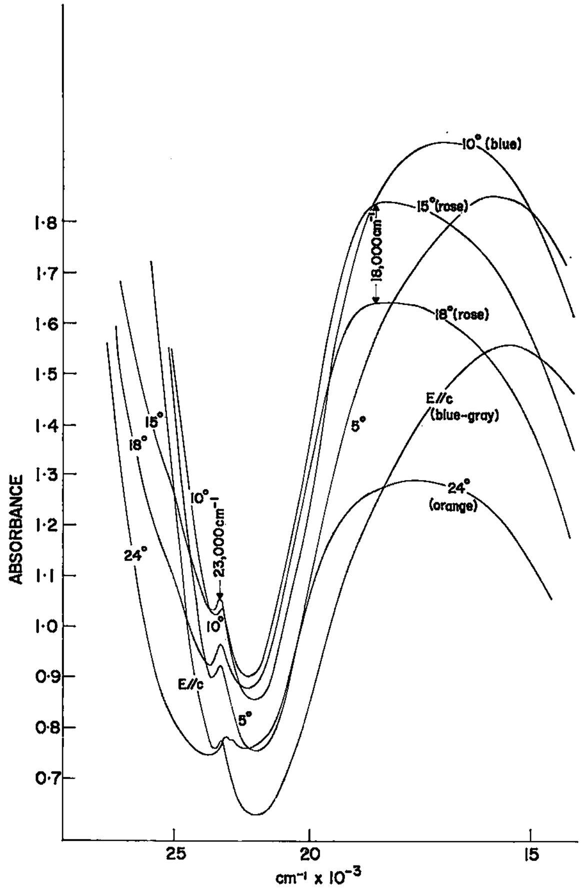


FIG. 5. Spectra of a relatively thick (~.004–~.005 cm) *a-c* section of riebeckite measured with electric vector at indicated angles to *c*-direction.

but are not presented here. These were found to be similar to all the other amphibole spectra of this study in that the main feature of each is a polarized band containing two components, with the one at higher energy (~19,000 cm^{-1}) being approximately half as intense as the one at lower energy (~15,500 cm^{-1}). However, the glaucophane and crossite spectra, (like those of holmquistite) differ from those of the calcic amphiboles and riebeckite in that the direction of *E* giving maximum intensity of the absorption envelope is essentially coincident with *c*. Also, for a given thickness of sample, the intensity of the UV-centered background absorp-

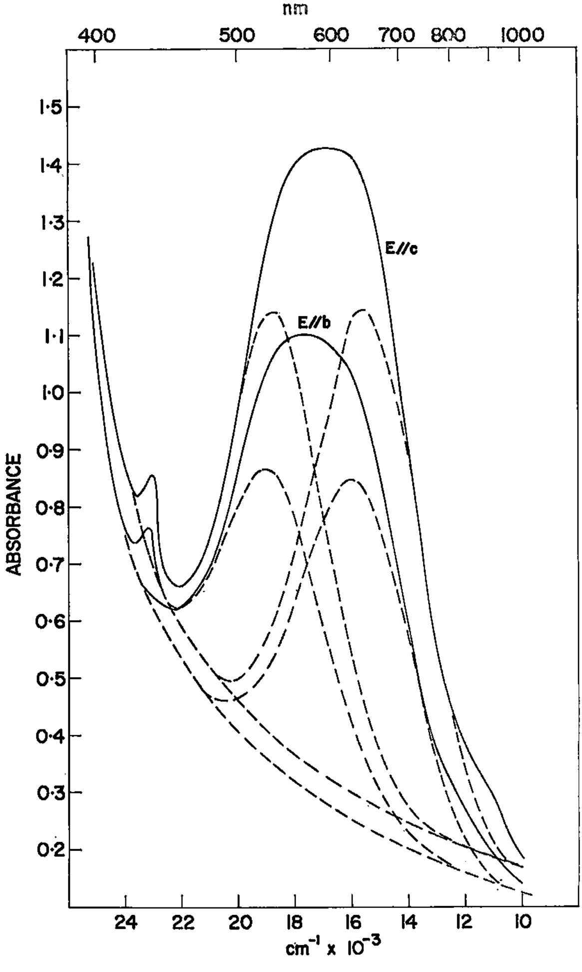


FIG. 6. $E//b$ and $E//c$ spectra of a b-c section of holmquistite; thickness of section ~.008 cm.

tion (absorption edge) is less intense than in the spectra of riebeckite and the calcic amphiboles (Figs. 5 and 8).

The spectra of all the alkali amphiboles of the present study show a minor sharp peak or shoulder at approximately 23,000 cm^{-1}. Such a feature has been noted previously in the spectra of many Fe-bearing silicates, including riebeckite (Manning & Nickel 1969) and glaucophane (Bancroft & Burns 1969), and is most likely due to the $^6A_1 \rightarrow {}^4A_1E(G)$ transition of Fe^{3+}. The band (shoulder) is not seen in the spectra of the

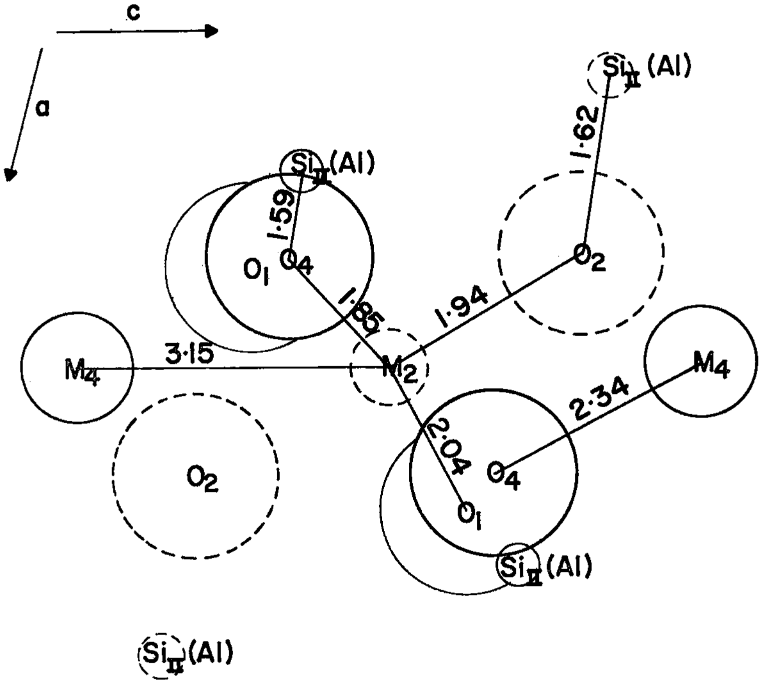


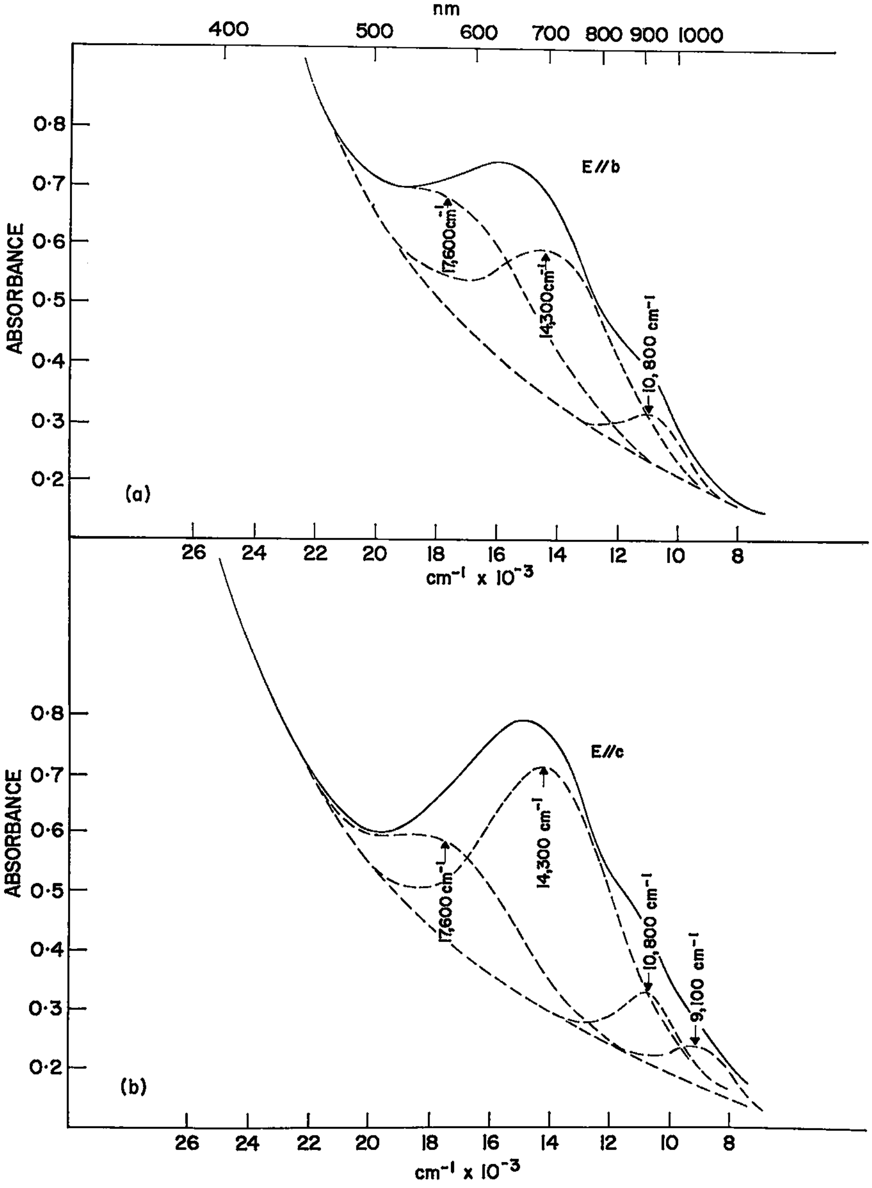
FIG. 7. Bond distances between centers associated with $O^{2-} \rightarrow Fe^{3+}(M_2)$ charge-transfer. The distances are those for glaucophane (Papike & Clark 1968). For clarity the distances between centers has been doubled. The fractional y-coordinates are as follows:
$O_1 = 0.09$; $O_2 = 0.17$; $M_2 = 0.18$; $Si_{II}(Al) = 0.17$ and 0.34; $O_4 = 0.25$; $M_4 = 0.28$.

calcic amphiboles, no doubt because it is "obscured" by the more intense absorption edge of these minerals.

INTERPRETATION OF SPECTRA

The principal absorption band has already been ascribed to intervalence charge-transfer between adjacent Fe^{2+} and Fe^{3+} ions. This assignment is strongly supported by the observation that, for the spectra of *a-c* sections of all the amphiboles studied, the band has zero intensity when E is $\perp c$, *i.e.* the direction in which the component of the M–M vector is zero. Because there are two components in the band, this suggests the interaction of Fe^{2+} and Fe^{3+} on two different pairs of cation sites.

Recently, much has been done in attempts to establish cation site-occupancy for sodic amphiboles, *e.g.* crocidolite (Burns & Prentice 1968),



FIGS. 8a and 8b. *E//b* and *E//c* spectra, respectively, of a *b*-*c* section of ferrohastingsite; thickness of section ~.003 cm.

TABLE 1. CHEMICAL ANALYSES AND LOCATIONS OF AMPHIBOLE SPECIMENS

	Riebeckite, St. Peter's Dome Colorado	Holmquistite, Uto, Sweden	Ferrohastingsite, York River, Bancroft, Ont.	Barkevikite, Tvedalen, Norway	Hornblende, Fission Mine, Wilberforce, Ont.
Source of Analyses, or Analyst	Borg (1967)	Sundius (1947)	D. C. Harris[a]	D. C. Harris[a]	D. C. Harris[a] R. Craig[b]
SiO_2	49.87	59.58	37.53	40.12	
TiO_2	0.34	0.02	2.44	2.13	
Al_2O_3	1.04	7.19	8.58	6.77	8.18[a]
Fe_2O_3	14.25	9.35	20.8 } %Fe	18.9 } %Fe	7.20[b]
FeO	20.19	4.88			15.80[b]
MnO	1.22	0.41	1.00	1.30	
MgO	0.03	11.66	4.12	5.20	
CaO	0.44	0.06	7.61	9.68	9.78[a]
Na_2O	7.75	0.50	4.32	3.43	
K_2O	1.15	0.27	2.22	1.69	

a = Electron probe } this laboratory.
b = Chemical }

glaucophane (Papike & Clark 1968), holmquistite (Whittaker 1969), glaucophane, crossite and riebeckite (Bancroft & Burns 1969; Strens 1970). From this work it is clear that, for monoclinic amphiboles at least, the M_4 site is occupied preferentially by alkali metal ions and that the M_1 and M_3 sites are enriched in Fe^{2+} while M_2 is enriched in Fe^{3+}. Assuming that such a distribution of cations prevails for the amphiboles whose spectra are given in Figs. 3, 4, 5, 6 and 8, it is reasonable to assign the more intense, low-energy component (14,300–16,000 cm^{-1}) primarily to the interaction $M_1(Fe^{2+}) \rightarrow M_2(Fe^{3+})$ and the weaker, high-energy component (17,500–19,000 cm^{-1}) to $M_1(Fe^{2+}) \rightarrow M_3(Fe^{3+})$ or $M_3(Fe^{2+}) \rightarrow M_1(Fe^{3+})$ interaction. Structural positioning of the metal ions (Fig. 2) precludes the possibility of either component being due to charge-transfer between ions on adjacent M_3 and M_2, or M_1 and M_1, sites because such a transition would have no intensity in the *b*-direction; however, it is obvious that both components are present in both the $E//c$ and $E//b$ spectra.

The polarization properties of the two components have either not been recognized by previous workers, (Chesnokov 1961; Manning & Nickel 1969) or have been misinterpreted, at least in part (Littler & Williams 1965; Hush 1967; Bancroft & Burns 1969).

Based on absorbance (above background) values taken from the spectra of Figs. 3b, 6 and 8, it is apparent that both $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer bands of $E//c$ spectra are 1.5–2.0 times as intense as those of $E//b$ spectra (this ratio applied as well to approximate oscillator strengths calculated for riebeckite). Such a range of values is consistent with the assignments made above because the M_1–M_2 and M_1–M_3 vectors, when resolved into directions parallel to *c* and *b*, have a theoretical $c{:}b$ ratio of 1.73:1.

It would be expected that the $Fe^{2+} \rightarrow Fe^{3+}$ absorption envelope should have its maximum intensity when $E//c$ because this is the most favourable direction for the electric vector of the radiation field to interact with overlapped t_{2g} orbitals on adjacent iron ions. However, this condition is so only for glaucophane, crossite, holmquistite and very thin sections of riebeckite; that it does not apply to the spectra of the calcic amphiboles and relatively thick sections of riebeckite, will be explained subsequently.

For a symmetrical electron-transfer process such as that being considered here, the energy of the $Fe^{2+} \rightarrow Fe^{3+}$ transition is dependent on both the separation of the interacting centers and the frequency of their lattice vibrations, (Hush 1967 p. 424). Therefore, considering interionic distances only (Fig. 2), the 3,000–4,000c m^{-1} energy difference between the proposed $M_1(Fe^{2+}) \rightarrow M_2(Fe^{3+})$ and $M_1 \overset{\rightarrow}{\underset{\leftarrow}{\text{or}}} M_3$ transitions is rather large; however, the coordination spheres of the M_1, M_2 and M_3 sites are non-equivalent chemically and geometrically and, consequently, the frequency of lattice vibrations associated with each site may be appreciably different.

The distance (3.2 Å) between adjacent M_2 and M_3 or M_1 and M_1, sites is somewhat large; however, the interaction between Fe^{2+} and Fe^{3+} on these sites could give rise to a relatively weak band(s) in the near ultraviolet region. Such a band would likely be "swamped" by the absorption edge and be completely polarized in the *b* direction. As we will see, only in the $E//b$ spectra of the calcic amphiboles (Fig. 8) is there evidence for such preferential absorption.

Recently, it has been proposed by Strens (1970) that the appearance of the two components in the $Fe^{2+} \rightarrow Fe^{3+}$ absorption envelope is in some way related to the distortion of the M_2 octahedron in which virtually all the Fe^{3+} in the monoclinic alkali amphibole is thought to be contained. However, because Fe^{3+} has a symmetrical $^6A_1$ ground state, the presence of two acceptor levels in the Fe^{3+} ion with a separation of 3,000–4,000 cm^{-1} especially for electron transfer via t_{2g}-t_{2g} orbital overlap, is considered unlikely.

Having proposed a model to explain the two $Fe^{2+} \rightarrow Fe^{3+}$ electron-transfer bands, it is necessary to account for the variation in their relative intensities and attempt to correlate this to cation site-occupancy data obtained by previous workers.

Cation ordering and band intensities

Using Mössbauer and infrared spectroscopic techniques, Bancroft & Burns (1969) have established that in crocidolites and glaucophanes of low-temperature, high-pressure origin, cations are highly ordered with the majority of Fe^{3+} and Al^{3+} ions occurring in M_2 positions. The Fe^{2+} and Mg^{2+} ions are concentrated in M_1 and M_3 positions. In glaucophanes (and crossites) there is relative enrichment of these ions in M_3 positions, whereas the Fe^{2+} ions are enriched in M_1 positions of crocidolite. However, in high-temperature riebeckite, such as that from Colorado, Bancroft & Burns have found that the cations are more randomly distributed. According to Burns (private communication) it is possible that as much as 25% of the Fe^{3+} in such riebeckite may be distributed between the M_1 and M_3 sites.

The intensity of the 17,600–18,000 cm^{-1} band ($M_1 \underset{\leftarrow}{\overset{\rightarrow}{\text{or}}} M_3$ interaction) of the riebeckite spectra in Fig. 3, like those of corresponding bands of crossite and glaucophane, seems to be anomalously intense if only 25% or less of the Fe^{3+} is distributed between M_1 and M_3. The raw spectra suggest that approximately one third of the Fe^{3+} could be present on these sites. The spectra in Fig. 5 indicate that the intensity and shape of the $Fe^{2+} \rightarrow Fe^{3+}$ absorption envelope of the riebeckite spectra seem to be strongly influenced by the intensity of the UV-centered absorption band. Indeed, Fig. 5 indicates that the intensity of the upper component, assigned to charge-transfer between M_1 and M_3, is probably enhanced relative to that of the lower-energy components ($M_1 \rightarrow M_2$) by some form of "intensity borrowing". On this basis, then, the observed intensity of the band at 17,600–18,000 cm^{-1} can be made compatible with a combined M_1-M_3 site-occupancy of $<25\%$ of the total Fe^{3+}.

It is important to note that, although there are twice as many M_1 and M_2 sites as M_3 sites per unit cell, each Fe^{3+} on an M_3 site can interact potentially with an Fe^{2+} ion on four adjacent M_1 sites, *i.e.* twice the number for Fe^{3+} on M_1 or M_2.

Influence of $O^{2-} \rightarrow Fe^{3+}$ charge-transfer

The "absorption edge" is the low-energy wing of a broad, intense, absorption band due mainly to the $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer process (*e.g.* Marfunin *et al.* 1969). Of all the possible $\text{O}^{2-} \rightarrow$ metal-ion charge-transfer processes of importance in ferromagnesian silicates, $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ occurs at the lowest energy ($\sim$40,000 cm^{-1}). It is to be expected that the absorption edge should become more intense and "encroach" on the visible region as the specimen thickness increases; this is indeed evident from a comparison of the riebeckite spectra in Figs. 4 and 5. That the 18,000 cm^{-1}-component of the spectra of the blue-grey area (Fig. 5) overlaps with the absorption edge to a greater extent than does the lower energy component ($M_1 \rightarrow M_2$), is undoubtedly responsible for the unequal rates of change in the intensity of these features as the section is rotated in polarized light. In the spectra of the thinner blue area of the same material (Fig. 4) the extent of band mixing or overlap (as indicated by the breadth of the "valley" in Figs. 4 and 5) is such that the intensity of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ bands are affected in such a way by the $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer process, that only the intensity, and not the nature, of the color changes.

Because Fe^{3+} is predominantly on M_2, the $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ absorption envelope in the ultraviolet is due to a composite of charge-transfer transitions from O_1, O_2 and O_4 oxygens (Figs. 1 and 7) to Fe^{3+} on this site. (For our present purpose we choose to ignore the weaker contributions associated with Fe^{3+} on other sites.) Using the formal charges on the ions forming the coordination sphere of O_1, O_2 and O_4, it can be shown by the electrostatic valency principle of Pauling (1929) that O_1 carries a deficiency of 0.16 electron with respect to its ideal charge of -2, while O_2 and O_4 carry an excess of 0.04 and 0.37 electronic charges respectively. Thus the net difference in favour of $\text{O}^{2}{}_{4}{}^{-} \rightarrow \text{Fe}^{3+}(M_2)$ charge-transfer is approximately 0.2 electronic units. That such a charge transfer should predominate over others is to be expected also on the basis of the relatively short O_4–M_2 distance of 1.85 Å compared with 1.94 Å and 2.04 Å for O_2–M_2 and O_1–M_2 respectively, (Papike & Clark 1968).

If it is assumed that all O^{2-}–$Fe^{3+}(M_2)$ bonds are identical, then the resultant of the projections of the six bonds on *a-c* makes an angle of ~40° with the *c*-axis. However, bond distances and the formal charges on O_1, O_2 and O_4 are not equal, therefore the direction in which the absorption due to $O^{2-} \rightarrow Fe^{3+}$ charge-transfer should have its maximum intensity cannot be calculated from simple considerations.

Comments on the spectra of holmquistite, crossite and glaucophane

On the basis of electron-density measurements, Whittaker (1969) concluded that the M_2 site of his holmquistite was nearly completely occupied by Al^{3+} and, that Fe^{2+} and Fe^{3+} were distributed between M_1 and M_3 only. However, the spectra of our Swedish holmquistite (Fig. 6) are not consistent with such a distribution of iron, since the shape of the absorption envelope implies the combination of two Gaussian curves. Using the model proposed above for riebeckite, it is necessary to conclude that iron occurs on M_2 as well as M_1 and M_3, but because the 19,000 cm^{-1} component ($M_1 \overset{\rightarrow}{\underset{\leftarrow}{\text{or}}} M_3$ charge transfer) is of approximately the same intensity as the low-energy component ($M_1 \rightarrow M_2$) it is probable that there is proportionally more iron distributed between M_1 and M_3 than in the Colorado riebeckite. Although they are not presented here, the spectra of a crossite and a glaucophane specimen were found to be qualitatively similar to those of holmquistite, *i.e.* with the principal pleochroic band having maximum intensity when $E//c$. As before, such a property is to be expected for amphibole spectra dominated mainly by $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer via overlap of t_{2g} orbitals having projections in the *c*-direction.

In general, the Fe^{3+} contents of holmquistite, glaucophane and crossite are significantly lower than that of riebeckite. Therefore, it is to be expected that for a given specimen thickness, the visible regions of their absorption spectra will be influenced less than those of riebeckite by $O^{2-} \rightarrow Fe^{3+}$ charge-transfer. Thus, the kind of pleochroic effects shown in Fig. 5 are not observed for the monoclinic amphiboles glaucophane and crossite. It is of interest to note that, in contrast to riebeckite, extinction parallel to *c* is observed in *a-c* sections of glaucophane and crossite. However, it is suggested that if the polarized spectra of sufficiently thick specimens of these varieties could be measured, they would be essentially the same as those of riebeckite; similarly, lack of extinction would be detected.

It has been mentioned previously that the intensity of the upper $Fe^{2+} \rightarrow Fe^{3+}$ band ($\sim$19,000 cm^{-1}) of glaucophane and crossite spectra is somewhat higher than expected on the basis of site-occupancy studies (Papike & Clark 1968; Bancroft & Burns 1969; Strens 1970). This apparent inconsistency with the proposals made above is somewhat awkward but it must be concluded, tentatively at least, that the intensity-borrowing mechanism is still strong enough to enhance the $M_1 \underset{\leftarrow}{\overset{\rightarrow}{\text{or}}} M_3$ band relative to the main $M_1(Fe^{2+}) \rightarrow M_2(Fe^{3+})$ band at lower energy.

Calcic amphiboles

The spectra of the barkevikite and hornblende specimens (Table 1) were qualitatively similar to those of the ferrohastingsite shown in Fig. 8. The major difference between the spectra of the alkali and calcic amphiboles is that the absorption edge of the latter extends into the visible region to a greater extent than in the former, and as a result there is greater overlap with the $Fe^{2+} \rightarrow Fe^{3+}$ absorption envelope. Also, for *a-c* sections of the calcic amphiboles, the angle between *c* and the direction giving maximum absorbance was appreciably greater (14–28°) than for the Colorado riebeckite (10°). This also correlates with a correspondingly greater deviation from parallel extinction for these specimens.

Although the Fe^{3+} content is known only for the hornblende of this work (Table 1), other published analyses of calcic amphiboles (Deer, Howie & Zussman 1963) indicate that it is generally lower than in riebeckites, for example. Therefore, it is necessary to account for the greater intensity of the $O^{2-} \rightarrow Fe^{3+}$ charge-transfer absorption of calcic amphiboles relative to that in the spectra of the alkali amphiboles.

It is known that there is considerable substitution of aluminum for silicon in calcic amphiboles (Deer, Howie & Zussman 1962). Again, using Pauling's electrostatic valency principle, it can be calculated that such substitution in the Si_{II} tetrahedra (Figs. 1 and 8), coupled with the replacement of Na^+ by Ca^{2+} on M_4, results in O_4 and O_2 having excess electronic charges of 0.50 and 0.17 respectively, while O_1 has a charge close to the ideal of -2. Thus, on the basis of such considerations, it is understandable that the $O^{2-} \rightarrow Fe^{3+}(M_2)$ charge-transfer band is much more intense in the spectra of the calcic amphiboles than in those of the alkali varieties.

That the background absorption in the $E//b$ spectra of calcic amphiboles is significantly more intense than in the $E//c$ spectra (Fig. 9) may represent the combined effect of $M_3(Fe^{2+}) \rightarrow M_2(Fe^{3+})$ and $M_1(Fe^{2+}) \rightarrow M_1'(Fe^{3+})$ charge-transfer in the *b*-direction. Because the indicated transitions likely occur $\geq$25,000 cm^{-1} their intensities are possibly enhanced to a much greater extent than in corresponding alkali amphiboles by "mixing" with the $O^{2-} \rightarrow Fe^{3+}$ charge-transfer process which is more intense for the calcic amphiboles than for the alkali amphiboles.

The green hues of the calcic amphiboles are a direct consequence of the absorption of violet-blue light ($O^{2-} \rightarrow Fe^{3+}$ charge-transfer) and red-orange light ($Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer).

Some Comments on the Pleochroic Scheme and Anomalous Extinction in Amphiboles

As pointed out above, the direction of maximum absorption in the monoclinic amphiboles does not coincide with the crystallographic *c*-axis, as would be the case if the absorption in the visible portion of the spectrum were due entirely to $Fe^{3+} \rightarrow Fe^{2+}$ charge-transfer: deviation of the direction of maximum absorption from *c* was attributed to the influence of the $O^{2-} \rightarrow Fe^{3+}$ charge-transfer band that extends into the visible part of the spectrum from the UV region. The pleochroic scheme, therefore, although determined by the structure, as predicted by de Bethune & Jans (1966), is related to the *c*-crystallographic axis in a very complicated fashion that can at present only be evaluated qualitatively. It is even difficult to determine the direction of maximum absorption with any precision, because the multiple bands that constitute the absorption spectrum change in relative intensity as the section is rotated on the microscope stage. For this reason no attempt has been made to put the pleochroic scheme on a quantitative basis.

The work has, however, shed some light on the phenomenon of anomalous extinction that is commonly observed in certain amphiboles, and which has, in certain cases, been attributed to elliptical polarization (Shoda 1958; Nickel & Mark 1965). It now appears that the elliptical polarization in the amphiboles, and in some other highly pleochroic minerals, is very likely due to the non-coincidence of the principal optical and absorption directions.

Examination of the amphiboles in this study, and the reports of previous workers, shows that there is anomalous extinction in sections close to (010), but not in sections normal to (010), *i.e.* parallel to the *b* crystallographic axis. This indicates that the major divergence of the vibration and absorption directions is in the (010) plane, which is not surprising in view of the optical properties of monoclinic crystals: One of the principal optical directions coincides with the *b* axis, and the other two principal optical directions are in the (010) plane, but not fixed relative to the *a* and *c* axes. It appears that the principal absorption directions are similarly related to the crystallographic axes, but that they do not coincide with the vibration directions in the (010) plane.

Of the monoclinic amphiboles examined in this study, the riebeckite, hornblende, barkevikite and ferrohastingsite showed a marked lack of extinction in *a-c* sections, which indicates a substantial difference between the positions of the vibration directions and the principal absorption directions in the (010) plane. The other monoclinic amphiboles—crossite and glaucophane—appeared to exhibit normal extinction, which suggests that the principal vibration and absorption directions in these minerals are nearly, or completely coincident.

Attempts were made to measure the angle between the principal vibration and absorption directions in the sections that showed the anomalous extinction, but it was not possible to determine the positions of the principal vibration directions with sufficient precision to give consistent and meaningful results. Nonetheless, the relationship between the crystal structure, optical indicatrix, and absorption indicatrix is a very interesting one, and merits further investigation.

ACKNOWLEDGMENTS

The authors are grateful to Drs. R. G. Burns and M. G. Townsend for helpful and stimulating discussions. Thanks are also due to Dr. D. C. Harris for microprobe analyses, to Mr. R. R. Craig for chemical analyses, and to Mr. P. O'Donovan for assistance in preparing the mineral sections.

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Manuscript received December 12, 1969, emended January 22, 1970