ON THE ORIGIN OF 'REVERSE PLEOCHROISM' OF A PHLOGOPITE*

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ABSTRACT

The visible spectra of phlogopite with a reversely pleochroic scheme consist essentially of three bands in the 450–550 mμ region superimposed on the wing of a strongly pleochroic band centred in the ultraviolet region. The spectra have their greatest intensity when polarized light vibrates normal to the cleavage plane, the reverse of micas with normal pleochroic schemes. By comparing the phlogopite spectra with those of an iron orthoclase and $FeCl_4^-$, materials which are known to contain tetrahedrally-coordinated Fe^{3+}, it has been established that the three-band system in the visible region is also due to this ion. The background absorption is considered to be due to an $O^{2-} \rightarrow Fe^{3+}$ charge-transfer band which is most intense when the vibration direction is coincident with the O^{2-} (unbridged)–Fe bond perpendicular to (001) in the iron-bearing tetrahedra.

INTRODUCTION

Recent studies in the Mines Branch laboratory have been devoted to an understanding of the origin of colour and pleochroism in ferromagnesian silicates (Faye, 1968, 1968*a*; Faye, Manning and Nickel, 1968). It was shown, for example, that the pleochroism of phlogopite, biotite and chlorite with normal schemes can be directly related to the electronic interaction of Fe^{2+} and other ions in the octahedral layer parallel to the cleavage plane (Faye, 1968*a*). A pre-requisite for this kind of interaction is the overlapping of lobes of the t_{2g} set of d orbitals of adjacent ions sharing octahedral edges. The pleochroism of the sheet silicates was found to be strongly influenced by the $Fe^{2+} \rightarrow Fe^{3+}$ interaction, and it was suggested (Faye, Manning and Nickel, 1968) that this might be among the more important and widespread causes of pleochroism in ferromagnesian silicates.

The so-called normally pleochroic micas exhibit their most intense absorption spectrum when the electric vector (E) of polarized light vibrates in a direction parallel to (001)–(E$\|$(001)). The E$\|$(001) spectra are essentially the same in all directions. Expressed in terms of absorption parallel to the principal vibration directions, $X < Y \approx Z$.

Recently the authors had occasion to measure the polarized absorption spectra of a red-brown phlogopite from Old Chelsea, Québec, which

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exhibited marked reverse pleochroism, *i.e.*, a pleochroic scheme in which the E $\perp$ (001) spectrum is more intense than the E$\|$(001) spectrum. Because of the apparent conflict with the previous interpretation of the normal pleochroism of the sheet silicates (Faye, 1968*a*) it was decided to examine the spectra of the Chelsea phlogopite in detail with the object of understanding the processes responsible for its pleochroism.

The literature reveals that Grum-Grzhimailo and Rimskaya-Korsakova (1964) studied a phlogopite with "anomalous inverse absorption spectra" and concluded that this is due to the presence of Fe^{3+} in tetrahedral sites substituting for Al, but other than stating that "a light ray oscillating at right angles to the cleavage plane encounters more iron ions than is the case in the N_gN_m plane and is, therefore, absorbed more intensely" they did not attempt to explain the mechanism(s) responsible for the pleochroism.

EXPERIMENTAL

Old Chelsea Phlogopite

The specimens were obtained from the Petrology Collection of the University of Ottawa as thin sections (~0.003 cm) mounted on glass slides. Sections were cut from specimens taken from the contact of dolomitic marble (possibly carbonatite) and aplite from McLoskey's field, approximately 5½ miles northwest of Old Chelsea, Québec. A brief description of the geology of these rocks was given by Hogarth (1966). *X*-ray and optical studies revealed that the phlogopite is normal meroxene of the 1 M structure type with optic orientation $Y = b$, dispersion $v > r$, $2V_x = 8°$, and "in plane" absorption $Y > Z$ (barely apparent in thick sections). To obtain the spectra of transverse ($\perp$(001)) and basal or cleavage sections, areas of suitable size and known orientation were selected and masked with black ink. The chemical analysis of the Old Chelsea phlogopite is given in Table 1.

Templeton Phlogopite:

This material and its polarized spectra (Fig. 2) have been described previously (Faye, 1968*a*).

Measurement of Spectra:

All spectra were measured at room temperature with a Beckman DK-2A recording spectrophotometer and the experimental details are similar to those reported previously (Faye, 1968*a*).

In measuring the spectra, Polaroid film was used as the polarizer. Because the film is ineffective at wavelengths >800 mμ, all spectra in Figs. 1 and 2 are unpolarized beyond 800 mμ.

TABLE 1. CHEMICAL ANALYSIS OF OLD CHELSEA PHLOGOPITE
ANALYST—H. B. WIIK, HELSINKI

	Weight, per cent		Atoms based on 44 positive charges	
Na_2O	0.46	Na	0.128	1.954
K_2O	9.79	K	1.795	
CaO	0.20	Ca	0.031	
MgO	26.05	Mg	5.582	6.097
MnO	0.05	Mn	0.006	
TiO_2	0.17	Ti	0.018	
FeO	4.08	Fe^{2+}	0.491	
Al_2O_3	9.97	Al	1.689	7.925
SiO_2	41.37	Si	5.948	
Fe_2O_3	2.66	Fe^{3+}	0.288	
		O	19.488	24.446
H_2O	4.15	OH	3.980	
F	2.15	F	0.978	
Total	101.10			
less O ≡ F	0.91			
	100.19			

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 per litre 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 the possible overlapping of neighbouring bands.

In calculating the molar concentration of Fe^{2+} and Fe^{3+} in the Chelsea phlogopite, it was assumed that its density was 3 g/ml.

POLARIZED ABSORPTION SPECTRA OF OLD CHELSEA PHLOGOPITE

Fig. 1 shows the $E \perp X$ and $E \| X$ spectra of the Old Chelsea phlogopite. It is immediately apparent that the pleochroic scheme of this specimen is the reverse of that of the Templeton phlogopite whose polarized spectra are shown in Fig. 2. The spectra in Fig. 1 also show that there are two sources of visible pleochroism: the sloping wing of the intense background absorbance centered in the ultraviolet region, and the bands centered at 19200, 20300 and 22700 cm^{-1} which are superimposed on the background absorption.

The $E \perp X$ spectrum of the Old Chelsea phlogopite results in a pale orange-brown colour which is due to progressively decreasing absorption of violet to yellow-green light in the 400–600 mμ region. The relatively

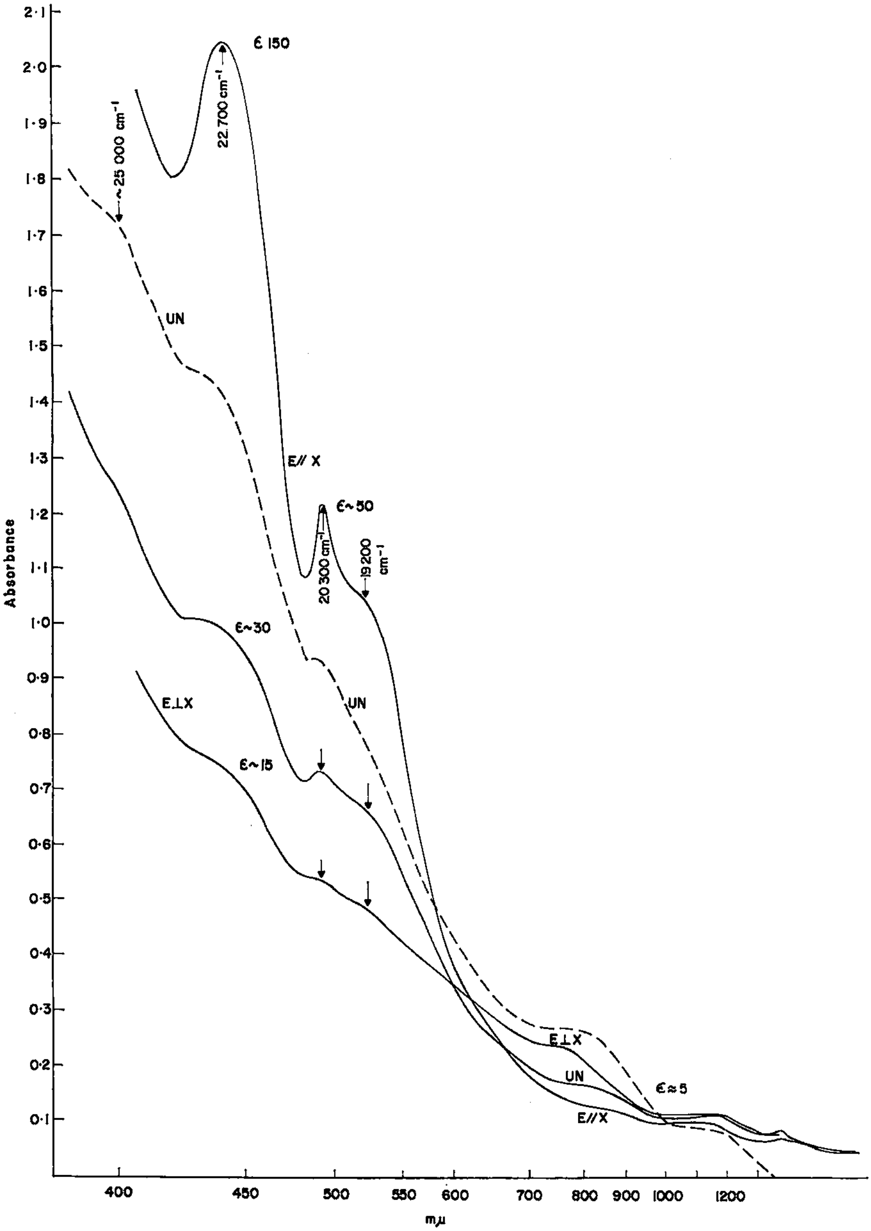

FIG. 1. Polarized and unpolarized (UN) spectra of transverse section of Old Chelsea phlogopite, thickness $\sim 10^{-3}$ cm; UN—curve is that of a basal section.

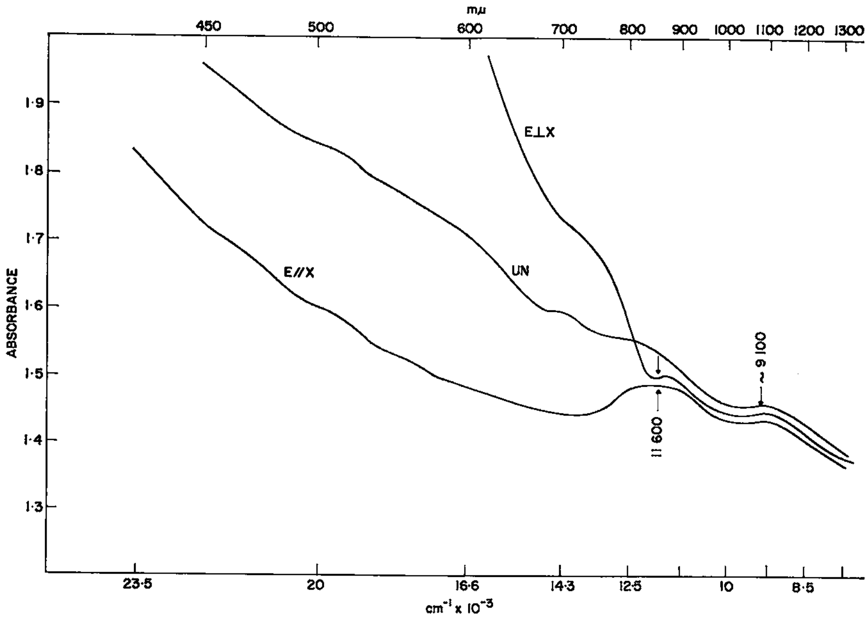

FIG. 2. Polarized and unpolarized (UN) spectra of a transverse section of Templeton phlogopite; thickness 0.056 cm.

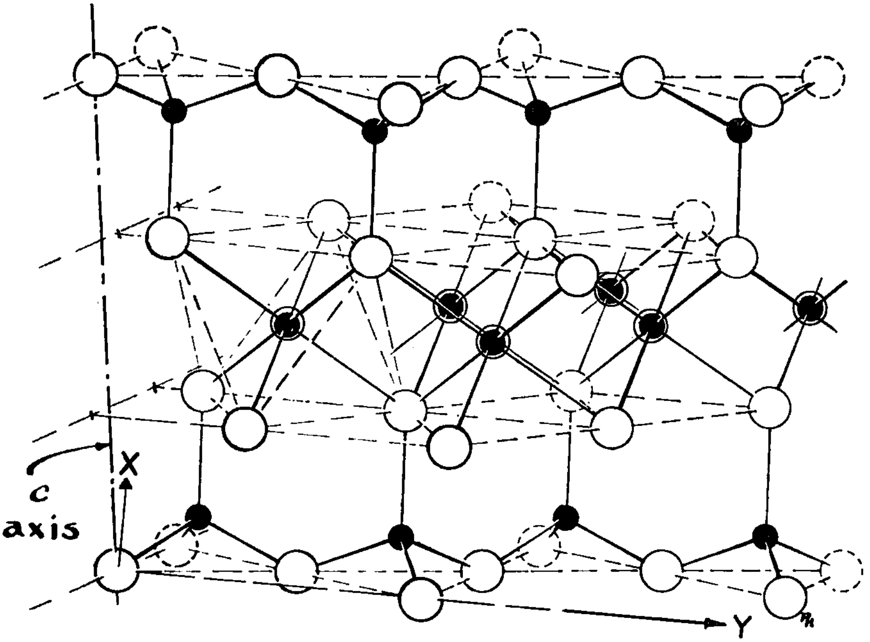

FIG. 3. Part of the structure of phlogopite; modified after Berry and Mason (1959); black circles represent Fe^{3+}, Si^{4+}; ringed black circles represent Fe^{2+}, Mg^{2+}.

intense red-brown colour associated with the E||X spectrum is largely due to the strong absorption of blue-green in the 450–550 mμ region together with more intense background absorption of the shorter wavelengths. In other words, the transmission of the residual red, orange and yellow gives rise to the red-brown colour.

The minor shoulders between 700 and 1200 mμ in the spectra of Fig. 1 are similar to corresponding bands in the spectra of the Templeton phlogopite (Figure 2) and in other sheet silicates (Faye, 1968, 1968*a*); their origin will be discussed below. Because these features lie outside the visible region (400 to 700 mμ) they do not contribute to the colour of the phlogopite.

INTERPRETATION OF SPECTRA OF OLD CHELSEA PHLOGOPITE

Evidence for Octahedral Fe^{2+}

It is well established that Fe^{2+} is present in octahedral sites in the sheet silicates and that the $^5T_2 \rightarrow {}^5E$ transition gives rise to two bands in the 9000 to 12000 cm^{-1} (~800–1100 mμ) region of the absorption spectra. Each band has an extinction coefficient, ϵ, approximately in the 2–7 litre/mole·cm range (Faye, 1968, 1968*a*).

Although poorly defined, such a band (shoulder) system is present in the spectra of Fig. 1 and therefore it is confidently assigned to pseudo-octahedrally coordinated Fe^{2+}. This assignment is supported by the fact that the estimated unpolarized extinction coefficient is approximately 5 litre/mole·cm, a value consistent with that found for other micas (Faye, 1968).

It has been mentioned previously that the pleochroism of phlogopites, biotites, chlorites etc. with normal schemes, is influenced by the electronic interaction of adjacent Fe^{2+} and Fe^{3+} in the octahedral layers lying parallel to (001). Such interaction is manifested by a polarized or pleochroic absorption band centered around 14000 cm^{-1} (700 mμ). It is reasonable, then, to suggest that the more intense absorption of the E ⊥ X spectrum in the 650–950 mμ region is due to $Fe^{2+} \rightarrow Fe^{3+}$ interaction. It is to be emphasized again that this effect is so weak that it does not affect the visible pleochroism in the phlogopite specimen under study. Although the concentrations of both Fe^{2+} and Fe^{3+} are appreciable (3.2 and 1.9% respectively) the weakness of the $Fe^{2+} \rightarrow Fe^{3+}$ interaction is a direct indication that the number of interacting ions in the octahedral layer is very low.

Evidence for Tetrahedral Fe^{3+}

From previous studies on the absorption spectra of the sheet silicates (Faye, 1968, 1968*a*) it is known that both octahedrally coordinated

Fe^{2+} and Fe^{3+} give rise to relatively weak ($\epsilon \sim 0.1$ to 2.0 litre/mole·cm) features in the visible region due to so-called spin-forbidden transitions.

The prominent bands at 19200, 20300 and 22700 cm^{-1} in the $E \| X$ spectrum of Fig. 1 are very similar in energy to certain of those assigned to octahedral Fe^{2+} in biotite and chlorite spectra (Faye, 1968*a*); however, their intensities based on total iron, are 1–2 orders of magnitude higher than the latter, therefore they cannot be attributed to Fe^{2+}. Indeed, if such an assignment were made it would also be necessary to accept that spin-forbidden bands would be much more intense than those assigned to the spin-allowed bands ($\epsilon \sim 5$ litre/mole·cm) of the $^5T_2 \rightarrow {}^5E$ transition of octahedral Fe^{2+}.

The *d–d* spectrum of Fe^{3+} in an octahedral environment contains a number of low-intensity features ($\epsilon < 3$ litre/mole·cm) including an especially sharp and prominent band at approximately 22000–23000 cm^{-1} (*e.g.*, andradite (Manning, 1967), vesuvianite (Manning, 1968) and muscovite (Faye, 1968)). This band has been assigned to the field-independent $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition of octahedrally coordinated Fe^{3+}. In no case known to the authors has this band been found to be pleochroic in the manner of the 22700 cm^{-1} band of the Old Chelsea phlogopite spectra. Therefore, because of the pleochroic nature of the 22700, 20300 and 19200 cm^{-1} bands of this phlogopite and their anomalously high intensities, especially in the $E \| X$ spectrum, it is unlikely that they are due to Fe^{3+} in the octahedral layer of the mineral.

Having excluded the probability that the three pleochroic bands are due to Fe^{2+} or Fe^{3+} in the octahedral layer, it is reasonable to consider that they may be due to Fe^{3+} in tetrahedral sites in the manner suggested by Grum-Grzhimailo and Rimskaya-Korsakova (1964). Indeed, this suggestion is consistent with the results of Mössbauer studies on Old Chelsea phlogopite which reveal the presence of tetrahedrally coordinated Fe^{3+} (Brown and Hogarth, in preparation). Also, it is known that Fe^{3+} may completely replace Al^{3+} in phlogopite (Steinfink, 1962) and thus, in the case of the Old Chelsea phlogopite, it seems necessary for the purposes of charge balance, to assume that Al^{3+} has been partially replaced by Fe^{3+} because Table 1 indicates that the Al^{3+} content is unusually low. It is also noteworthy that synthetic phlogopite in which Fe^{3+} proxies entirely for aluminium also exhibits the phenomenon of reverse pleochroism (Veres, Merenkova and Ostrovskii, 1955; Wones, 1963).

Recently, the detailed absorption spectrum of tetrahedrally bonded Fe^{3+} in an iron orthoclase has been recorded and transition assignments made for the spectral features (Faye, 1968*b*). Therefore, it is convenient to compare the orthoclase spectrum to that of the Old Chelsea phlogopite with the object of making transition assignments for the spectral features of the latter. It is to be noted that Grum-Grzhimailo and Rimskaya-Korsakova (1964) also used the spectrum of an iron orthoclase for comparison purposes.

In the orthoclase spectrum (Table 2) there are three principal features, the most intense of which was assigned to the field-independent $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition of tetrahedrally coordinated Fe^{3+}. It follows, therefore, that the 22650 cm^{-1} and 24000 cm^{-1} bands are due to the $^6A_1 \rightarrow {}^4T_1(G)$ and $^6A_1 \rightarrow {}^4T_2(G)$ transitions respectively (Faye, 1968*b*).

By analogy then, it is reasonable to assign the 22700, 20300 and 19200 cm^{-1} features of the Old Chelsea phlogopite spectra to the $^6A_1 \rightarrow {}^4A_1{}^4E$, $\rightarrow {}^4T_2$ and $\rightarrow {}^4T_1$ transitions respectively. As supporting evidence for these assignments it is of interest to note (Table 2) the similarity of the energy separations of the transitions of the phlogopite spectrum with the corresponding ones of the spectra of orthoclase and the $FeCl_4^-$ ion (Ginsberg and Robin, 1963), both materials containing Fe^{3+} in tetrahedral coordination.

TABLE 2. ENERGY SEPARATION (Δ) OF SPECTRAL TRANSITIONS OF MATERIALS CONTAINING TETRAHEDRAL FE^{3+}

Transition	Phlogopite	δ cm^{-1}	Orthoclase	δ cm^{-1}	$FeCl^{-4}$ in acetone (measured by author G.H.F.)	δ cm^{-1}
$^6A_1 \rightarrow {}^4A_1{}^4E(G)$	22700		26500		18700	
		2400		2500	16700	2200
$\rightarrow {}^4T_2(G)$	20300		24000		16300	
		1100		1350	14700	1100
$\rightarrow {}^4T_1(G)$	19200		22650		14100	

That the transitions appear at disparate energy levels in the three materials is certainly due to a shift of the field-independent terms relative to the free ion values. Depression of the free ion term values is considered to be indicative of covalent bonding (Ginsberg and Robin, 1963).

As stated previously, the optical pleochroism of the Old Chelsea phlogopite is obviously related to the large change in intensity of the spin-forbidden *d–d* bands of tetrahedrally coordinated Fe^{3+} and the background absorption from the ultraviolet region as the orientation of the mineral section is changed in polarized light. To account for these changes it is necessary to consider the manner in which the Fe^{3+}-tetrahedra are oriented in the phlogopite structure (Fig. 3).

It is accepted that the red-brown colour of many ferric compounds is due primarily to the low-energy wing of ligand → Fe^{3+} charge-transfer processes centered in the ultraviolet region (Fyfe, 1964; Cotton and Wilkinson, 1962). Thus the background absorption of the Old Chelsea phlogopite spectrum (Fig. 1) is probably due to $O^{2-} \rightarrow Fe^{3+}$ charge transfer.

From Fig. 3 it is evident that each Fe-tetrahedron is linked to an apex of an octahedron by a unique Fe^{3+}-O(unbridged) bond that is perpendicular to (001). Because this is the only bond in the phlogopite structure (excluding Al and Si tetrahedra) that is orthogonally related to the principal optical directions, it is logical to assume that the intensity of the ultra-violet-centered background absorption should be most intense in the $E\|X$ spectrum of Fig. 1, as observed. The charge-transfer absorption is also of appreciable intensity in the $E \perp X$ spectrum; this can be accounted for by the magnitude of the resultants of the projections of the remaining three Fe^{3+}-O(unbridged) bonds in directions parallel to (001).

A somewhat more perplexing problem is posed by the anomalously high intensity of the spin-forbidden *d–d* bands of Fe^{3+} at 22700, 20300 and 19200 cm^{-1} in the $E\|X$ spectrum of Fig. 1. These bands, because they are due to sextuplet → quadruplet transitions, are expected to be of modest intensity as in the orthoclase spectrum (Faye, 1968*b*). It is to be noted, however, that because of the mixing of *d* and *p* orbitals, spectral intensities for tetrahedrally coordinated ions are in general appreciably greater than for corresponding octahedrally coordinated ions (Cotton, 1963, p. 237).

Tentatively, it is suggested that the enhanced intensity of the Fe^{3+} bands in the $E\|X$ spectrum relative to those of the $E \perp X$ spectrum, of Fig. 1, is due to the greater degree of coupling (vibronic) between electronic and vibrational states when the electric vector of the radiation vibrates normal to the cleavage plane. It is not difficult to imagine that the stretching mode of the Fe^{3+}-O(unbridged) bond, $\perp$001, might influence the spectrum to a greater extent than corresponding modes of the three Fe–O(bridge) bonds.

CONCLUSION

We conclude that the present work describing the nature and origin of the reversely pleochroic phlogopite, is compatible with that previously made for the sheet silicates with normal pleochroic schemes (Faye, 1968*a*). Together, these works present consistent hypotheses about the pleochroism of the micas. It is to be noted however, that in cases where transition metal ions other than iron (*e.g.*, Cr^{3+}, Mn^{2+}, Mn^{3+}, Ti^{3+}) may be present in substantial concentrations, the spectra will differ appreciably from those studied above.

REFERENCES

BERRY, L. G. & MASON, B. (1959): *Mineralogy*. W. H. Freeman and Co. San Francisco, p. 503.

COTTON, F. A. (1963): *Chemical Applications of Group Theory*. Interscience Publishers, Inc., New York, p. 237.

COTTON, F. A. & WILKINSON, G. (1962): *Advanced Inorganic Chemistry*. Interscience Publishers, Inc., New York, p. 715.

DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1963): *Rock Forming Minerals*, vol. **4**. Longman, Green and Co. Ltd., London.

FAYE, G. H. (1968): The optical absorption spectra of certain transition metal ions in muscovite, lepidolite, and fuchsite. *Can. J. Earth Sci.* **5**, 31–38.

——— (1968*a*): The optical absorption spectra of iron in six-coordinate sites in chlorite, biotite, phlogopite and vivianite. Some aspects of pleochroism in the sheet silicates. *Can. Mineral.* **9**, 403–425.

——— (1968*b*): The optical absorption of tetrahedrally bonded Fe^{3+} in orthoclase. *Can. Mineral.* **10**, this issue.

FAYE, G. H., MANNING, P. G. & NICKEL, E. H. (1968): The polarized optical absorption spectra of tourmaline, cordierite, chloritoid and vivianite: ferrous–ferric electronic interaction as a source of pleochroism. *Amer. Mineral.* **53**, 1174–1201.

FYFE, W. A. (1964): *Geochemistry of Solids*. McGraw-Hill Book Co., New York, p. 168.

GINSBERG, A. P. & ROBIN, M. B. (1963): The structure, spectra, and magnetic properties of certain iron-halide complexes. *Inorg. Chem.* **2**, 817–822.

GRUM-GRZHIMAILO, S. V. & RIMSKAYA-KORSAKOVA, O. M. (1964): Absorption spectra of phlogopite holding trivalent iron in fourfold coordination. *Dokl. Akad. Nauk SSSR* **156**, 123–125.

HOGARTH, D. D. (1966): Intrusive carbonate rocks near Ottawa Canada. *Mineral. Soc. India, I.M.A. Vol.*, 45–53.

MANNING, P. G. (1967): The optical absorption spectra of some andradites and the identification of the $^6A_1 \rightarrow {}^4A_1{}^4E$ (G) transition in octahedrally bonded Fe^{3+}. *Can. J. Earth Sci.* **4**, 1039–1047.

——— (1968): Optical absorption spectra of octahedrally bonded Fe^{3+} in vesuvianite. *Can. J. Earth Sci.* **5**, 89–92.

STEINFINK, H. (1962): Crystal structure of a trioctahedral mica: phlogopite. *Amer. Mineral.* **47**, 886–896.

VERES, G. I., MERENKOVA, T. B. & OSTROVSKII, I. A. (1955): Pure synthetic ferriginous hydroxy-mica. *Dokl. Akad. Nauk SSSR* **101**, 147–150.

WONES, D. A. (1963): Phase equilibria of "ferrianite" $KFe_3^{+2}\,Fe^{+3}\,Si_3O_{10}\,(OH)_2$. *Amer. J. Sci.* **261**, 581–596.

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