ON THE ORIGIN OF COLOUR AND PLEOCHROISM OF ASTROPHYLLITE AND BROWN CLINTONITE

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ABSTRACT

A spectral study is reported of the origin of colour and pleochroism in astrophyllite and brown clintonite. Sections of both minerals cut parallel and perpendicular to the 001 (cleavage) plane were examined in polarized light.

Astrophyllite and the brown clintonite show a non-pleochroic two-band system in the near-infrared region that is assigned to *d-d* transitions in octahedrally-bonded Fe^{2+}.

Both astrophyllite and clintonite exhibit a strong pleochroic absorption band in the blue end of the spectrum that is the obvious cause of colour and pleochroism of the minerals. The band is observed at 23,000 cm^{-1} in astrophyllite, and has maximum intensity when *E* coincides with the orientation of Ti-O-Ti units. The band is observed at 22,000 cm^{-1} in clintonite with maximum intensity when *E* coincides with the plane of *d*-orbital overlap between neighbouring cations in the octahedral layer. (*E* represents the vibration direction of the electric vector of incident light). In both minerals, the band is assigned to Ti^{3+}-Ti^{4+} electronic interaction.

INTRODUCTION

Although it has been known for many years that compounds containing a metal in two different valence states often exhibit intense colouration (Weyl, 1951; Martinet & Martinet, 1952), it is only in very recent times, with the advent of ligand-field theory, that the origin of the intense colour in some of these compounds has been determined. Two mixed-valence compounds of historical interest are Prussian blue and the mineral vivianite. Robin (1962) has measured the absorption spectrum of a suspension of Prussian blue, and he assigned a strong band at 14,000 cm^{-1} to an electronic transition from the t_{2g} orbital of Fe^{2+} to a t_{2g} orbital of Fe^{3+}. Hush (1967) assigned a strong band at 15,000 cm^{-1} in the spectra of partially-oxidized vivianite to $Fe^{2+} \rightarrow Fe^{3+}$ intervalence electron-transfer. Hush further concluded that the intense colours and pleochroism of many Fe-containing minerals may be due to Fe^{2+}-Fe^{3+} interaction in certain crystal directions.

Recent work in these laboratories, begun without foreknowledge of the work of Hush, has been concerned with the origin of pleochroism in silicate minerals in which neighbouring Fe^{2+} and Fe^{3+} ions share octahedral-octahedral or octahedral-tetrahedral edges. Atomic arrangements in the former case imply t_{2g}-t_{2g} *d*-orbital overlap and in the latter case,

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t_{2g}-e_g orbital overlap. It was suggested that a pleochroic absorption band, in the energy range 13,500 cm^{-1}–17,000 cm^{-1}, in the spectra of some sheet-silicates (Faye, 1968), tourmaline, cordierite and vivianite (Faye, Manning & Nickel, 1968) is due to an Fe^{2+}-Fe^{3+} intervalence electron-transfer process. The pleochroic band has maximum intensity when the electric vector of incident light vibrates in the same plane as the overlapping *d*-orbitals of the t_{2g} set of Fe^{2+} and Fe^{3+}; this plane is the 001 plane of tourmaline and the sheet-silicates. It is evident, therefore, that Faye, Manning & Nickel (1968) and Hush (1967) are in agreement as to the cause of the colouration and pleochroism in vivianite.

While it would seem from the foregoing discussion that there is strong evidence for Fe^{2+}-Fe^{3+} electronic interaction in some Fe-containing minerals, little is known of intervalence electron-transfer processes in minerals for other cations, e.g., Ti. However, Jorgensen (1957) has shown that a dimer Ti(III)·Ti(IV)Cl$_x$ absorbs strongly in 12 M HCl at 21,000 cm^{-1}, and he concluded that the band was due to Ti^{3+}-Ti^{4+} interaction. There seems no obvious reason why Ti^{3+}-Ti^{4+} interactions should not occur in silicate minerals, provided that geometrical considerations are favourable, e.g., t_{2g}-t_{2g} orbital overlap. For this reason, a spectral study is reported of the origin of pleochroism in Ti-containing brown clintonite and astrophyllite. Clintonite is a trioctahedral brittle mica (Forman, 1951; Forman, Kodama & Maxwell, 1967), while astrophyllite has a structure (Woodrow, 1967) closely related to that of biotite except that the tetrahedral Si layer also contains octahedrally-coordinated Ti ions. Of especial interest is the fact that the pleochroic schemes for the two minerals are different (Table 1), astrophyllite showing maximum light absorption in $E \perp (001)$ spectra and clintonite maximum absorption in $E /\!/ (001)$ spectra. The symbol E represents the vibration direction of the electric vector of incident light.

TABLE 1. PLEOCHROIC SCHEMES OF SECTIONS OF ASTROPHYLLITE AND CLINTONITE CUT $\perp$(001)

	$E /\!/ (001)$	$E \perp (001)$	Cleavage
Astrophyllite	yellow	reddish-orange	(001) perfect
Clintonite	reddish-brown	yellow-brown	(001) perfect

MATERIALS

Good crystalline specimens of astrophyllite and brown clintonite were obtained from Mr. H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada. The clintonite came from Amity County, New York, while astrophyllite came from St. Peter's

Dome, Pike's Peak, El Paso County, Colorado. The latter mineral has been completely analysed by König (1877) (Table 2), but for safety's sake, the reported values for Ti and total Fe were checked in these laboratories by Mr. R. Craig.

TABLE 2. CHEMICAL ANALYSIS AND UNIT CELL CONTENT OF EL PASO ASTROPHYLLITE

Group	Metal Oxide %		Unit Cell Content		Theoretical cell content
A	Na_2O	2.54	1.059	2.434	3.00
	K_2O	5.01	1.375		
	FeO	26.10	4.695		
B	Fe_2O_3	6.56	1.062	6.555	7.00
	MgO	0.30	0.096		
	MnO	3.48	0.634		
	CuO	0.42	0.068		
	TiO_2	13.58	2.197		
C	Ta_2O_5	0.80	0.047	2.475	2.00
	ZrO_2	2.20	0.231		
D	Al_2O_3	0.70	0.177	7.636	8.00
	SiO_2	34.68	7.459		
X	OH		5.079	31.000	31.00
	O		25.921		

EXPERIMENTAL DETAILS

Absorption spectra of cleavage sections and sections cut perpendicular to the 001 plane were obtained using either Cary-14 or Beckman DK-2A double-beam spectrophotometers. The dimensions of the crystals were at least 2 mm × 1 mm (length × breadth). In the visible region, polarized spectra were obtained by placing matched Polaroid sheets in both sample and reference beams, while Nicol prisms were used in the near infrared. All spectra were taken at room-temperature.

Sections of astrophyllite and clintonite cut perpendicular to the 001 plane were prepared by first immersing crystal slabs in a clear, colourless hard-setting cement and then cutting the hardened block in the desired orientation with a 0.003 in. tungsten wire saw. The crystals, supported by a disc of cement, were thinned to the desired degree and polished.

Cleavage sections of both astrophyllite and clintonite are non-pleochroic, but sections $\perp$(001) are markedly pleochroic. In this paper, therefore, are reported polarized-light spectra of sections $\perp$(001), and unpolarized-light spectra of sections $/\!/$(001).

The extinction coefficient of a band is given by

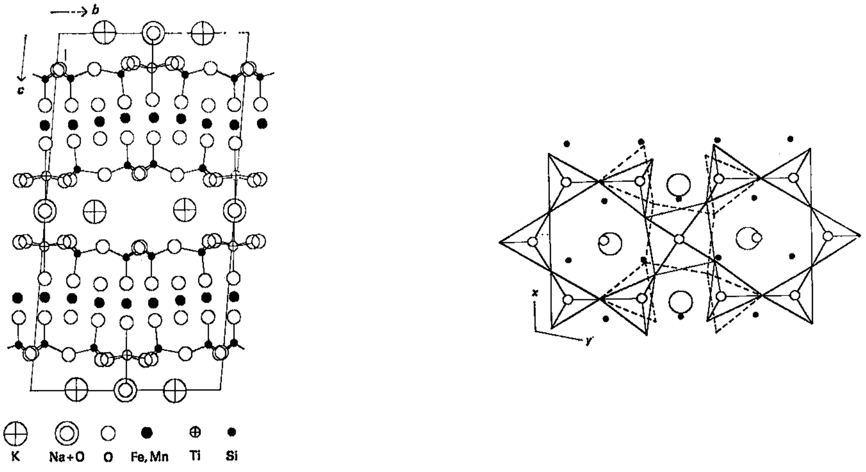
$$\epsilon = \frac{A}{C \times l},$$

where A is the absorbance of the band, C is the cation concentration in moles/litre and l is the thickness of the section in cm. The units of ϵ are therefore litres/mole-cm.

DISCUSSION

Structures of astrophyllite and clintonite

The structure of astrophyllite $(K,Na)_3(Fe,Mn)_7Ti_2Si_8(O,OH)_{31}$, has recently been described by Woodrow (1967). The basic unit of astrophyllite consists (Fig. 1) of a continuous sheet of $(Fe,Mn)O_6$ octahedra sandwiched between two sheets composed of chains of SiO_4 tetrahedra joined by TiO_6 octahedra. These multiple sheets are separated by alkali ions. According to Woodrow (1967), the Ti-O-Ti units lie in a plane that is very close to being perpendicular to the 001 plane.



(a) (b)

FIG. 1. Crystal structure of astrophyllite after Woodrow (1967). (a) is projection along the x axis. (b) is projection along [001] of one layer ($z = 0$ to $z = c/4$) of the structure. Black dots = Fe atoms at approximately $z = c/4$; large circles = alkali ions at $x = 0$; small circles = oxygen atoms. Dashed lines indicate an alternative arrangement.

Cations in the (Fe,Mn) octahedral layer of astrophyllite share octahedral edges in the same manner as described earlier for some sheet-silicates (Faye, 1968). The dimensions of the sites in the octahedral layer and the Ti sites of the Si/Ti layer have been calculated from the original parameters of Woodrow (1967) using a bond-and-angle-scan computer programme (Gabe, 1967). There are four Fe^{2+} sites, all with modest distortions from a regular octahedron. Bond lengths for a given octahedron vary from approximately 2.08 Å to 2.22 Å, and together with angular distortions, the highest site symmetry would seem to be C_2. Also, some of the coordinating anions may be OH. It is, of course, possible that distortions of this magnitude may not significantly complicate the Fe^{2+} spectra.

The Ti site is non-centrosymmetric with very irregular Ti-O distances and O-Ti-O angles. The Ti-O bond lengths range from 1.80 Å to 2.30 Å, which, together with irregular bond angles, gives the site very low symmetry.

Clintonite, $Ca_2(Mg, etc._{4.6}Al_{1.4})Si_{2.5}Al_{5.5}O_{20}(OH)_4$, is a trioctahedral brittle mica that is related to phlogopite by the substitution of Ca^{2+} for K^+, some Al^{3+} for Mg^{2+} in the octahedral layer and, balancing all this, the substitution of Al^{3+} for Si^{4+} in the tetrahedral sites so that the Al:Si ratio is consistently as high as 2:1 (Deer, Howie & Zussman, 1962, p. 99). Chemical analyses of clintonites (Deer, Howie & Zussman, 1962, p. 99) show that they conform very closely in composition to the ideal formula of a trioctahedral mica, showing that, as in phlogopite, the octahedral sites are completely filled.

Cations in the octahedral layer of clintonite share octahedral edges in the same way as in phlogopite. Faye (1968) has assigned a pleochroic band at 14,000 cm^{-1} in phlogopite spectra, with maximum intensity when $E /\!/ (001)$, to Fe^{2+}-Fe^{3+} interaction in the 001 plane; the 001 plane contains the overlapping t_{2g}-t_{2g} orbitals of neighbouring Fe ions. Cation-cation interaction can therefore also be expected in the octahedral layer of clintonite.

The brown clintonite studied here contains 2.05% Fe and 0.3% Ti. Green clintonite can contain up to 2% Fe^{3+} and 1% Fe^{2+} in the same sample (Forman, Kodama & Maxwell, 1967), hence the brown colour of clintonites is probably due largely to Ti.

Some general remarks

The spectra of astrophyllite and clintonite (Figs. 2–5) are clearly dominated by a strong absorption band centred in the blue region at 22,000 cm^{-1}–23,000 cm^{-1}, which accounts mainly for the colour and pleochroism of the minerals.

The similar energies and shapes of the 22,000 cm^{-1} band in clintonite and the 23,000 cm^{-1} band in astrophyllite strongly suggest that they are of similar electronic origin. Because the astrophyllite contains 6% Ti, it seems reasonable to assign the bands to Ti. These bands are in no way reminiscent of Fe^{2+} *d-d* bands nor of $Fe^{2+} \rightarrow Fe^{3+}$ intervalence transfer

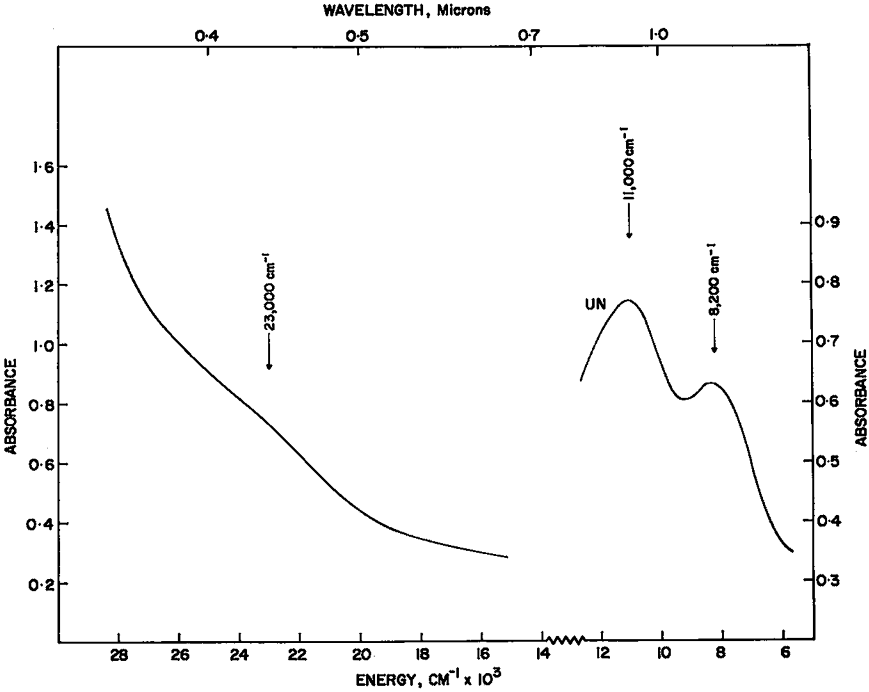


FIG. 2. Absorption spectrum of cleavage section of astrophyllite. Unpolarized light. Two halves of spectra are of crystals of different thickness.

bands studied earlier (Faye, Manning & Nickel, 1968). Neither are the bands characteristic of Mn^{2+} spectra with their sharp bands marking transitions to field-independent states (Manning, 1968). The bands would also seem to be at too high an energy for Mn^{3+} in octahedral sites in silicates, e.g., $\Delta = 13{,}450$ cm^{-1} for Mn^{3+} in epidote (Burns & Strens, 1967).

In this work it will be shown that the 22,000 cm^{-1}–23,000 cm^{-1} bands in astrophyllite and clintonite cannot be assigned to Ti^{3+} *d-d* transitions nor to O → Ti charge-transfer processes. A case will then be made for assigning the bands to Ti^{3+}-Ti^{4+} interaction.

Spectral features common to astrophyllite and clintonite

Both astrophyllite and clintonite exhibit two absorption bands in the near-infrared region, at 8,200 cm^{-1} and 11,000 cm^{-1} in astrophyllite (Fig. 2), and 9,000 cm^{-1} and 12,000 cm^{-1} in clintonite (Fig. 4). These bands very likely belong to octahedrally-bonded Fe^{2+} in both minerals. Two-band systems of this type have been observed in many Fe^{2+} com-

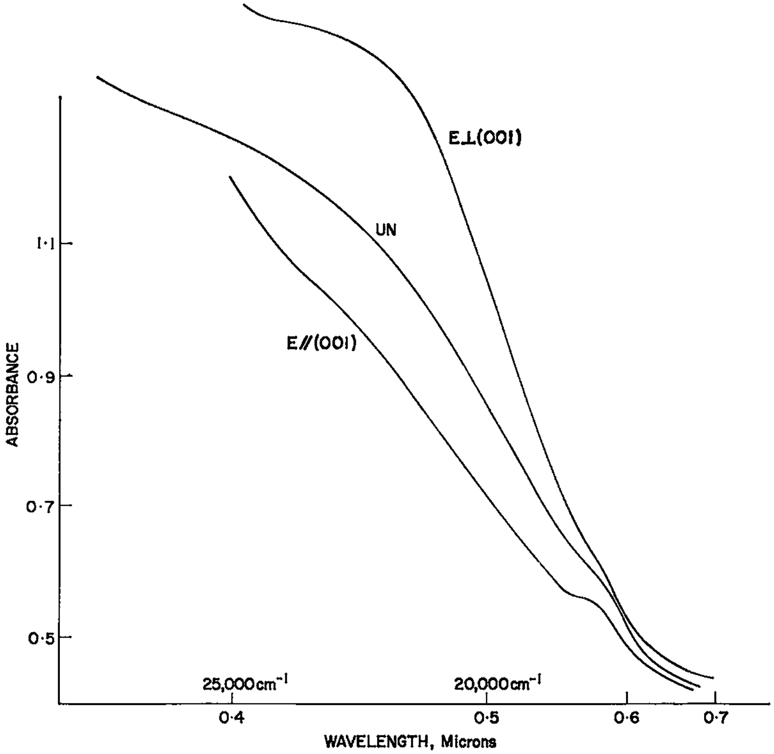


FIG. 3. Absorption spectrum of section of astrophyllite cut ⊥(001). l = ~0.03 mm.

pounds (Cotton & Meyers, 1960) and also for Fe^{2+} in sheet-silicates (Faye, 1968). The band may be assigned to the $^5T_2 \rightarrow {}^5E(D)$ transition in Fe^{2+}, the splitting being due to a dynamic Jahn–Teller (1937) mechanism arising from the uneven electron occupancy of the e_g orbitals in the excited ^5E state. This argument is strengthened by the earlier observation of two bands in the spectra of vivianite (Faye, Manning & Nickel, 1968), in which mineral Fe^{2+} is located in very-regular octahedral sites.

Because the two bands in the near-infrared region in astrophyllite and clintonite spectra are non-pleochroic, the effective symmetry of the Fe^{2+} site cannot be as low as C_2 (e.g., see Bancroft & Burns, 1967). Distortions of the octahedral site of the magnitude described for astrophyllite would therefore seem to have little influence on the nature of the Fe^{2+} spectra. The extinction coefficients of the Fe^{2+} bands in the astrophyllite and clintonite are ~5, indicating that the site distortion is relatively unimportant.

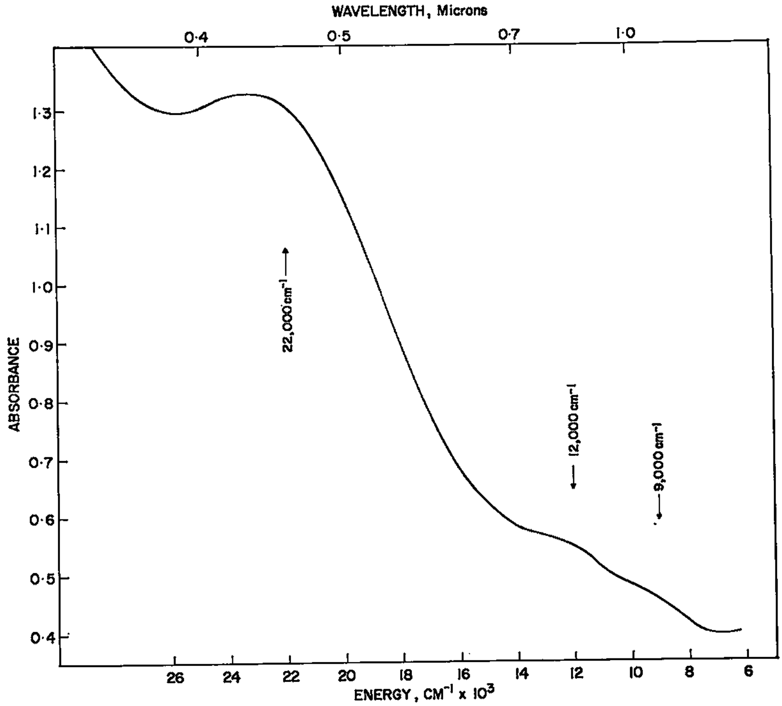


FIG. 4. Absorption spectrum of 001 section of clintonite in unpolarized light. $l = 0.05$ cm.

The unit-cell contents (Table 2) of the El Paso astrophyllite have been calculated by Nickel *et al.* (1964) from the analyses of König (1877). It is apparent that the astrophyllite shows marked deviations from the ideal $A_8B_7C_2D_8X_{31}$ formula. In order to fulfill basic structure requirements, it seems reasonable to place most of the Fe^{2+} in the octahedral layer, and the optical absorption spectra are not inconsistent with Fe^{2+} being in one type of octahedral site. Nickel *et al.* (1964) also put the appreciable amounts of Fe^{3+} in the octahedral layer.

Fe^{2+}-Fe^{3+} interaction in astrophyllite and clintonite

The origin of the weakly-pleochroic, or possibly non-pleochroic, band at 570 mμ (17,500 cm^{-1}) in astrophyllite spectra (Fig. 3) is of interest. Cations located in the octahedral layer of astrophyllite share octahedral edges with neighbouring cations of the layer, an arrangement that implies t_{2g}-t_{2g} orbital overlap. Faye (1968) and Faye, Manning & Nickel (1968) suggested that a strong, pleochroic band at ~14,000 cm^{-1} in the spectra

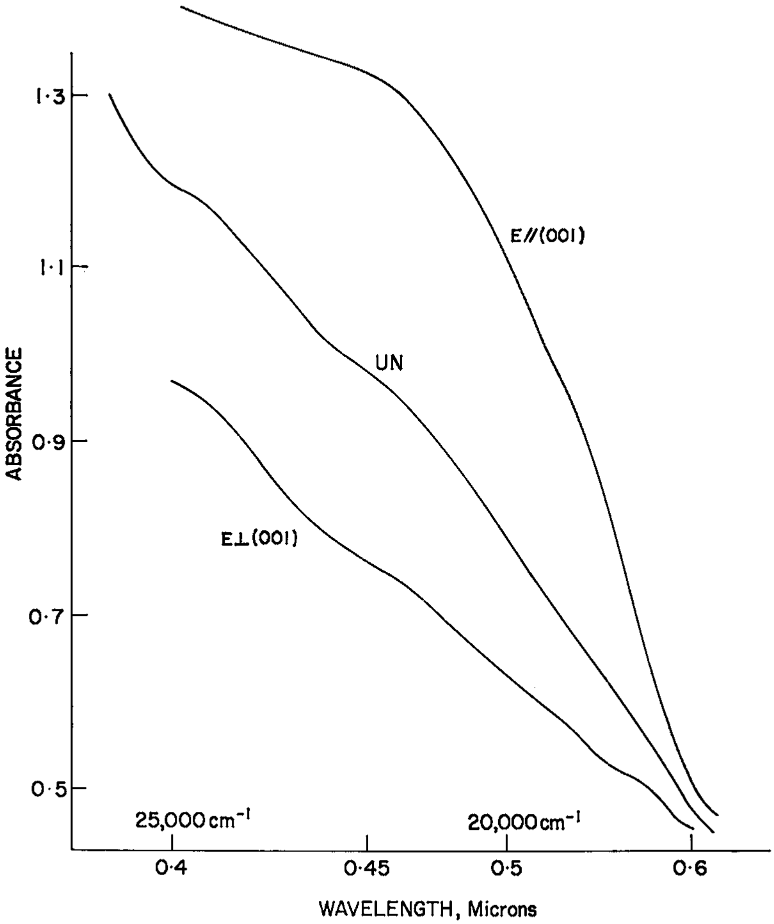


FIG. 5. Absorption spectrum of clintonite section cut ⊥(001) $l = \sim 0.03$ cm.

of some silicates, e.g., chlorite, biotite and tourmaline, is due to electron-hopping between Fe^{2+} and Fe^{3+} ions located in neighbouring octahedral sites in the 001 plane; and, correspondingly, the ~14,000 cm^{-1} band has maximum intensity in $E /\!/ (001)$ spectra.

Chemical analysis of the El Paso astrophyllite (Table 2) shows the presence of large amounts of both Fe^{2+} and Fe^{3+}, while the unit-cell contents (Table 2) indicate that, if both Fe^{2+} and Fe^{3+} are located in the octahedral layer, the probability of Fe^{2+}-Fe^{3+} interaction is very high, most certainly as high as in the sheet-silicates studied earlier (Faye, 1968) in which the concentrations of interacting Fe^{+2} and Fe^{3+} ions were generally considerably smaller. The absence of a strong, pleochroic band at ~14,000 cm^{-1} in astrophyllite spectra suggests that the Fe^{3+} ions are not located in the octahedral layer, but may substitute for Ti in the Si/Ti layer. The balancing of the unit-cell formula of astrophyllite depends on the accuracy of the Fe^{2+} and Fe^{3+} determinations, and bearing in mind the high Ti content of astrophyllite, this accuracy may not be high.

The spectrum of the brown clintonite (Fig. 4) does not show a pleochroic band at ~14,000 cm^{-1} that could be attributed to Fe^{2+} $\rightarrow$ Fe^{3+} electron-hopping. This suggests that the concentration of Fe^{3+} in the clintonite is very low. A pleochroic band at 14,700 cm^{-1} with maximum intensity in $E /\!\!/ (001)$ spectra, is easily observed in spectra of a green clintonite from Chichibu Mine, Saitama Prefecture, Japan. In general, the spectrum of this green clintonite is very similar to that of a chlorite studied earlier (Faye, 1968), in that two Fe^{2+} *d-d* bands are observed at 9,800 cm^{-1} and 11,800 cm^{-1}, while above 20,000 cm^{-1} the spectrum is dominated by spin-forbidden bands of Fe^{2+}. The spectra of the green clintonite and chlorite are sufficiently similar that there is little justification in reporting the former in detail.

The $^2T_2 \rightarrow {}^2E(D)$ *transition in* Ti^{3+}

The $^2T_2 \rightarrow {}^2E(D)$ transition in octahedrally-bonded Ti^{3+} has been observed in other silicate minerals, at 19,000 cm^{-1} in andradite (Manning, 1967) and 17,200 cm^{-1} in chloritoid (Faye, Manning & Nickel, 1968). It is possible that the 17,500 cm^{-1} band in astrophyllite spectra (Fig. 3) marks the $^2T_2 \rightarrow {}^2E(D)$ transition in Ti^{3+} since its energy is similar. The apparent pleochroism of the band may simply be due to the degree to which the 23,000 cm^{-1} band sweeps into the yellow region of the spectrum. Assuming that the ϵ-value of a Ti^{3+} band is ~20, the desired concentration of Ti^{3+} to account for its intensity is ~0.2%.

The absorption bands at 23,000 cm^{-1} in astrophyllite and 22,000 cm^{-1} in clintonite (Figs. 2–5) would seem to be at much too high an energy for Ti^{3+} *d-d* bands. Furthermore, if the 22,000 cm^{-1}–23,000 cm^{-1} bands did mark *d-d* transitions in Ti^{3+}, why are they so pronouncedly pleochroic in terms of intensity? In low-symmetry fields, the T_2 and E states are split, and at least two pleochroic bands at different energies would be expected (e.g., Bancroft & Burns, 1967). Alternatively, it is possible in astrophyllite, for example, that the t_{2g} electron in Ti^{3+} is localised in *d*-orbitals that have large projections on a plane perpendicular to (001). It can be readily deduced from Fig. 1 that one Ti *d*-orbital lies close to the 001 plane. However, none of the t_{2g} orbital lobes points directly towards a close-neighbouring cation, in which situation the orbital with lobes pointing directly towards a neighbouring cation would be preferentially occupied.

Oxygen → Ti charge-transfer bands

Oxygen → Ti^{3+} or Ti^{4+} charge-transfer bands were not observed in andradite (Manning, 1967) nor chloritoid (Faye, Manning & Nickel, 1968), which contained 5% Ti. In andradite, most of the Ti was present as Ti^{3+}. Furthermore, it is known that TiO_2, in which Ti is Ti^{4+}, is a white pigment. It would seem, therefore, that oxygen → Ti^{3+}/Ti^{4+} charge-transfer bands are relatively unimportant.

It is also difficult to see why the charge-transfer band in astrophyllite would be pleochroic. The two Ti-O distances (1.90 and 2.04 Å) perpendicular to (001) are not unique, the other four Ti-O distances being 1.80 and 1.91 Å (trans oxygens) and 2.14 and 2.30 Å.

Ti-O-Ti interaction in astrophyllite

The pleochroic schemes of biotite and astrophyllite are known to be different, biotite exhibiting maximum light absorption in $E /\!/ (001)$ spectra and astrophyllite in $E \perp (001)$ spectra. Because the main difference in the structures of the two minerals is the Ti-O-Ti units that lie perpendicular to (001) in astrophyllite, it seems logical to attribute the pleochroism of astrophyllite to these Ti-O-Ti units.

In discussing the light absorbing properties of these units, two situations will be considered, (i) the Ti ions of a Ti-O-Ti units are in the same valence state, i.e., either Ti^{3+} or Ti^{4+} and (ii) the Ti ions in a Ti-O-Ti unit are in different valence states, i.e., one is Ti^{3+} and the other Ti^{4+}.

Niobophyllite, the niobium analogue of astrophyllite, has been described by Nickel, Rowland and Charette (1964). Because of the similarity of the unit-cell parameters of niobophyllite and astrophyllite, the structures of the two minerals were presumed to be similar, with Nb^{5+} in niobophyllite replacing Ti^{4+} in astrophyllite. Considerations of ionic charge and ionic radius ($Nb^{5+} = 0.69$ Å; $Ti^{4+} = 0.68$ Å and $Ti^{3+} = 0.76$ Å) suggest that most of the Ti in astrophyllite is present as Ti^{4+}, otherwise very major differences in structure between astrophyllite and niobophyllite would occur. The 17,500 cm^{-1} band in astrophyllite has, earlier in this work, been assigned to the presence of a little Ti^{3+}.

Because Ti^{4+} is a $3d^0$ ion, the electron-transfer reaction

$$Ti^{4+} + Ti^{4+} \rightleftharpoons Ti^{5+} + Ti^{3+}$$

will likely only occur at very high energies. Therefore, it is unlikely that Ti^{4+}-Ti^{4+} interaction is the cause of the 23,000 cm^{-1} band in astrophyllite.

The electron-transfer reaction

$$Ti^{3+} + Ti^{3+} \rightleftharpoons Ti^{4+} + Ti^{2+}$$

will occur at much lower energies than the reaction described in the previous paragraph. However, the possibility that this reaction is the cause of the 23,000 cm^{-1} band in astrophyllite can be eliminated because a pleochroic band at this approximate energy is not observed in the spectra of two chloritoids that contain 2.5–5% Ti, mostly as Ti^{3+} (Faye, Manning & Nickel, 1968). Whether the Ti^{3+} ions are located in the brucite or corundum layers of chloritoid, direct t_{2g}-t_{2g} d-orbital overlap is possible within a given layer.

Let us now consider Ti^{3+}-Ti^{4+} interaction in Ti^{3+}-O-Ti^{4+} units in astrophyllite. This system is analogous to the Fe^{2+}-CN-Fe^{3+} system described by Robin (1962), who assigned a strong absorption at 14,000 cm^{-1} in the spectrum of Prussian blue to an electronic transition from the t_{2g} orbital of Fe^{2+} to a t_{2g} orbital of Fe^{3+}. Jorgensen (1957) has assigned a band at 21,000 cm^{-1} in the spectrum of a dimer, $Ti(IV)\cdot Ti(III)Cl_x$, formed in strong HCl solution, to $Ti^{3+} \rightarrow Ti^{4+}$ electron-transfer by way of an intermediate Cl^- ion. Hence, there would seem to be ample justification to assigning the 23,000 cm^{-1} band in astrophyllite to $Ti^{3+} \rightarrow Ti^{4+}$ electron-transfer through a common oxygen atom.

A possible orientation of the Ti t_{2g} orbitals and oxygen $p\pi$ orbitals is shown in Fig. 6. Even though the t_{2g} orbitals of the two Ti ions are directed towards each other, the Ti atoms are too far apart for direct d-orbital overlap. However, it is apparent that the $p\pi$ oxygen orbitals can bridge the t_{2g} orbital lobes. Any degree of Ti^{3+}-O covalency will lead to a spreading out of the Ti^{3+} t_{2g} electron over a volume encompassing the intermediate oxygen atom, thus leading effectively to Ti^{3+}-Ti^{4+} orbital overlap in the direction $\perp$(001). This would account for the pleochroism of the 23,000 cm^{-1} band in astrophyllite, since electron-transfer is possible perpendicular, but not parallel, to (001). If the $p\pi$ orbitals of the oxygen do overlap the t_{2g} orbital lobes of the Ti ions, then this would imply sp hybridisation of the intermediate oxygen, because the oxygen p-orbitals in higher coordination would otherwise be directed towards the Na and K ions (Fig. 1).

However, even if the oxygen p-orbitals are used in the coordination of oxygen to the alkali ions, $Ti^{3+} \rightarrow Ti^{4+}$ electron-transfer will occur with greatest probability when the Ti-Ti interorbital distance is least, i.e., when the Ti^{3+} d-electron is in one of the two t_{2g} orbitals lying in a plane $\perp$(001).

The intensity of the 23,000 cm^{-1} band in unpolarized light (Fig. 3) based on the total Ti concentration, is $\sim$40. This is likely to be a mini-

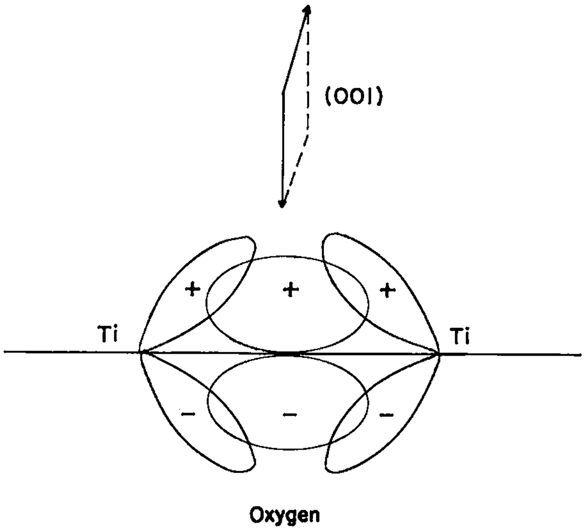


FIG. 6. Diagrammatic representation of possible orbital overlap between the t_{2g} d-orbitals of Ti (left and right portions of the diagram), and the $p\pi$ orbitals of oxygen (centre), in a projection ⫽(100).

mum ϵ-value for the $Ti^{3+} \rightarrow Ti^{4+}$ electron-transfer process because the calculation of the ideal value depends on the Ti^{3+} concentration and on each Ti^{3+} being adjacent to a Ti^{4+}.

Origin of pleochroism in clintonite

Cations located in the octahedral layer of sheet-silicates share octahedral edges, so that t_{2g}-t_{2g} orbital overlap occurs between neighbouring cations. A pleochroic absorption band at 14,700 cm^{-1} in E⫽(001) spectra of green clintonite has been assigned to Fe^{2+}-Fe^{3+} interaction (this work).

The possibility that the 22,000 cm^{-1} band in clintonite is due to interaction between neighbouring Ti^{4+}-Ti^{4+} or Ti^{3+}-Ti^{3+} ions may be eliminated in the same manner as for astrophyllite.

It is readily appreciated that the conditions for $Ti^{3+} \rightarrow Ti^{4+}$ electron-transfer are at their most favourable when there is direct d-orbital overlap. Bearing in mind the work of Hush (1967) and Faye, Manning & Nickel (1968) on $Fe^{2+} \rightarrow Fe^{3+}$ electron-transfer in vivianite, the assignment of the 22,000 cm^{-1} band in clintonite to direct $Ti^{3+} \rightarrow Ti^{4+}$ electron-transfer seems reasonable. The pleochroic properties of the band are readily explained: the band is most intense in E⫽(001) spectra because this is in the plane of *d*-orbital overlap. The 22,000 cm^{-1} band is very weak in $E \perp (001)$ spectra of clintonite, as expected.

Based on the total Ti concentration of 0.3%, the extinction coefficient of the 22,000 cm^{-1} band in clintonite in unpolarized light (Fig. 4) is ~50. The true extinction coefficient is very likely to be far greater than 50 because each Ti^{3+} ion may not be adjacent to a Ti^{4+} ion. It is not possible, at the present time, to obtain $Ti^{3+}:Ti^{4+}$ ratios in silicates from chemical analysis. Jorgensen (1957) measured a value of $\epsilon = 100$ for the intervalence transfer band in the chloride dimer.

Whilst this manuscript was being reviewed, Robbins and Strens (1968) published a paper in which they assigned pleochroic bands in the spectra of biotites, tourmalines, kyanite and glaucophane to $Fe^{2+} \rightarrow Fe^{3+}$ electron-transfer. The extinction coefficients of these bands were in the range 200–1000. Our ϵ-values for Ti are not inconsistent with this.

CONCLUSION

The origin of the colour and pleochroism of astrophyllite and brown clintonite has been attributed to Ti^{3+}-Ti^{4+} intervalence electron-transfer, via direct *d*-orbital overlap in the 001 plane of clintonite and via an intermediate oxygen atom in astrophyllite. The pleochroic properties of the main colour-producing absorption band in the blue region induced by the transition are consistent with the directions of *d*-orbital overlap.

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