

# ON THE ORIGIN OF COLOUR AND PLEOCHROISM IN ANDALUSITE FROM BRAZIL<sup>1</sup>

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## ABSTRACT

A study is reported of the polarized optical absorption spectra of a specimen of andalusite from Brazil. The weakly visible pleochroism of relatively thick  $a$ - $b$  sections is thought to be the result of variation in the intensity of a u.v.-centered band due to  $O^{2-} \rightarrow Fe^{3+}$  charge transfer. Arguments are presented to show why absorption is more intense in the  $E \parallel b$  spectrum. Intense pleochroism of andalusite sections containing the  $c$ -axis is considered to be the result of  $Ti^{3+} \rightarrow Ti^{4+}$  charge transfer via overlapping  $t_{2g}$  orbital lobes of adjacent ions located in the chains of octahedra that parallel the  $c$ -axis. Absorption is at a maximum when polarized light vibrates along the  $c$ -axis, the direction in which  $t_{2g}$  orbital overlap occurs.

## INTRODUCTION

Numerous studies have been made recently in this laboratory on the origin of colour and pleochroism of silicate and other minerals. From such work it is evident that, especially in ferromagnesium silicates,  $Fe^{2+} \rightarrow Fe^{3+}$  (Faye, 1968; Faye, Manning and Nickel, 1968) and  $Ti^{3+} \rightarrow Ti^{4+}$  (Manning, 1968*b*, 1968*c*) charge-transfer processes may be principal sources of pleochroism.

Recently, conflicting interpretations on the origin of pleochroism of blue kyanite (White and White, 1967; Robbins and Strens, 1968) have stimulated our interest in attempting to correlate the optical properties and structures of the various polymorphs of  $Al_2SiO_5$ .

Because andalusite has a much simpler structure than kyanite and because a good pleochroic specimen was available, it was decided to study first the polarized optical absorption spectra of andalusite with the object of explaining its colour and pleochroism.

## EXPERIMENTAL DETAILS

### *Preparation and Description of Andalusite Sections*

Andalusite from Brazil in the form of large fragments of single crystals, was obtained through the courtesy of H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada.

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Because of the easily identifiable external morphology of the andalusite fragments, sections containing the desired crystallographic axes were readily obtained by cuts made with a wire saw. All such sections (some mounted on microscope slides) were thinned to the desired thickness and polished by standard techniques prior to their spectral examination. The correct optical orientations of the completed sections were confirmed by optical interference figures obtained with a petrographic microscope. The sections used in the present work appeared to be free of inclusions.

### *Electron Probe Microanalysis of Andalusite Specimens*

Although each section was in itself reasonably uniform of colour or lack of it, there was considerable variation from section to section. For this reason each section was analyzed by electron-probe techniques for certain elements, particularly those that might influence its colour. The Materials Analysis Company (MAC) electron probe was operated at 25 kV for Fe and Ti and at 15 kV for Mg and Ca with a specimen current of 0.13  $\mu$ a and a beam diameter of approximately 30 microns for all specimens.

Because of the difficulty of obtaining standards with compositions close to that of andalusite, the analysis are subject to errors. For this work, a chemically analyzed muscovite containing 0.3% Ti and 4.5% Fe, a biotite with 1.88% Ti and 14.3% Fe, a synthetic  $\text{CaMgSi}_2\text{O}_6$  glass and MgO were used as standards. Several 100-second counts were made on each specimen and corrected for background which was determined by moving the spectrometer off peak. Linear inter- or extrapolations were then made from the standards. The limits of detections were considered to be 0.01% Fe, 0.01% Ti, 0.03% Mg and 0.01% Ca. The results are given in Table 1, together with the calculated extinction coefficients of the 20800  $\text{cm}^{-1}$  peak, and the orientation of the sections used to produce

TABLE 1. ANALYSES OF ANDALUSITE SECTIONS<sup>1</sup>

Section No.	Weight %			Extinction ( $\epsilon_{21}$ ) at 20800 $\text{cm}^{-1}$ , litre/mole·cm	Used for Measurement of	Thickness, cm
	Fe%	Ti%	Mg%			
1	0.4	0.08	0.06	—	E  a and E  b spectra	0.35
2	0.4	0.05	0.1	1000	E  c spectrum	0.06
3	0.5	0.1	0.1	400	" "	0.09
4	0.2	0.1	~0.03	130	" "	0.11
5	0.2	0.04	n.d.	170	" "	0.09
6	0.2	0.05	n.d.	145	" "	0.23
7	0.2	0.04	~0.03	240	" "	0.10
8 <sup>2</sup>	0.17	0.07				

<sup>1</sup>By one or more of electron probe, chemical and emission spectrographic analysis, Mn, Cr, V and Ca were found to be <0.02%.

<sup>2</sup>Chemical analysis of a large fragment.

the spectra. The net absorbance of the  $20800\text{ cm}^{-1}$  peak was taken to be the difference between that of the band maximum and that of the background which was assumed to extend under the band in a gaussian fashion.

All sections were examined spectrophotometrically and, for a given optical direction, all were similar qualitatively; therefore, the polarized spectra of only two are presented in Figs. 3 and 4.

#### *Measurement of Spectra*

All spectra were measured at room temperature with a Cary-14 spectrophotometer. A matched pair of Nicol prisms (each mounted in the well of a variable-aperture block assembly) were used to measure the polarized spectra. Approximate extinction coefficients (Table 1) were calculated from  $\epsilon = A/C \times l$ , where  $A$  is the absorbance, above background, of the band maximum;  $C$  is the concentration in moles/litre and  $l$  is the sample thickness in cm. In calculating  $C$  it was assumed that the density of andalusite was  $3.2\text{ gram/ml}$ .

## DISCUSSION

#### *Structure of Andalusite*

Half the aluminium ions in andalusite occur in Al-O octahedral groups that share edges with neighbours on either side and thereby form chains parallel to the  $c$ -axis (Figs. 1 and 2). The chains are linked internally by alternating tetrahedrally coordinated Si and bipyramidal five-co-ordinated Al (Figs. 1 and 2). The average octahedral Al-O<sub>6</sub> bond distance is  $1.94\text{ \AA}$  and the average bipyramidal Al-O<sub>5</sub> bond distance is  $1.84\text{ \AA}$ . The two Al-Al distances in the octahedral chains are  $2.69$  and  $2.87\text{ \AA}$  (Burnham and Buerger, 1961).

#### *Polarized Absorption Spectra of Andalusite*

##### *(a) Weak Pleochroism of $a$ - $b$ Sections*

Table 1 shows that the principal impurity in the Brazilian andalusite is iron. Electron spin resonance studies (Bil'dyukevich *et al.*, 1960; Holuj, Thyer and Hedgcock, 1966) have established that iron, as  $\text{Fe}^{3+}$ , substitutes for  $\text{Al}^{3+}$  mainly in the octahedral sites, chains of which extend along the  $c$ -axis.

The absorption spectrum due to  $\text{Fe}^{3+}$  in octahedral sites in silicate minerals has been fairly well documented (*e.g.*, Burns and Strens, 1967; Manning, 1967, 1968*a*). It is known that of the nine relatively weak spin-forbidden transitions from the sextuplet ground-state ( ${}^6\text{S}$ ) to states arising from the quadruplet terms of the free ion, only the lower four or

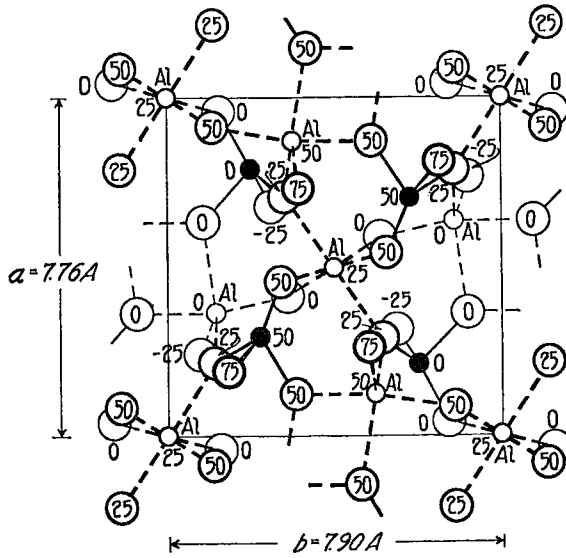


FIG. 1. The structure of andalusite viewed along the  $c$ -axis (after Bragg and Claringbull, 1965).

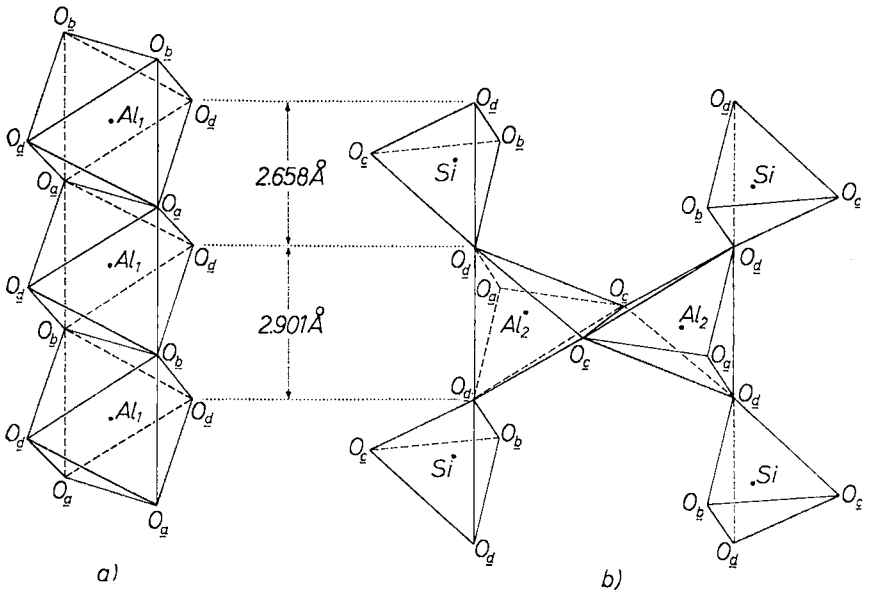


FIG. 2. Diagram of chains of coordination polyhedra parallel to the  $c$ -axis in the andalusite structure (after Burnham and Buerger, 1961).

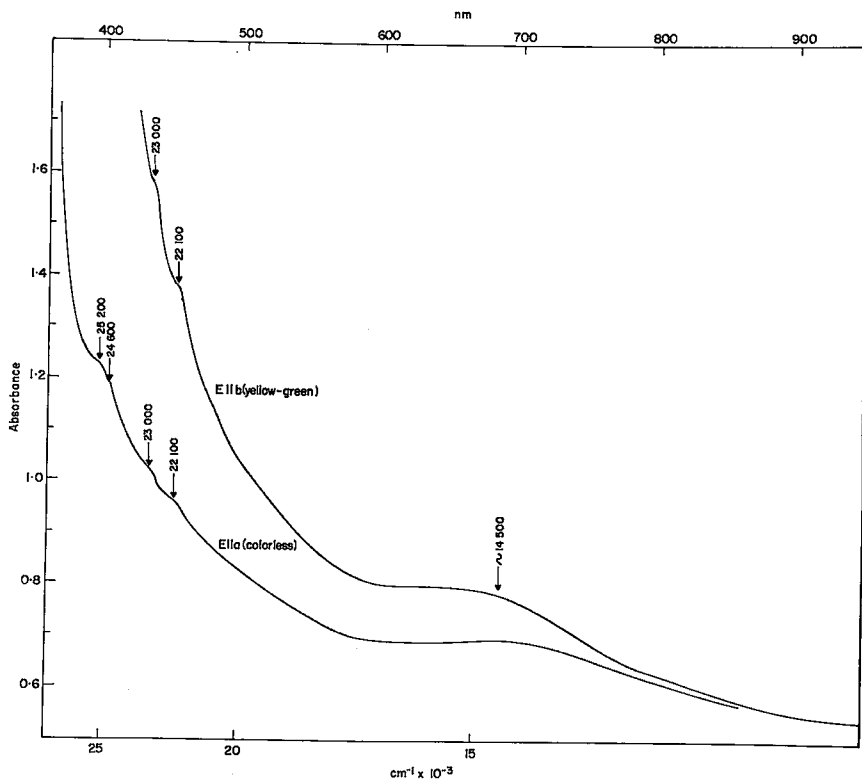


FIG. 3. Polarized spectra of  $a$ - $b$  in section 1 of andalusite, 0.35 cm thick.

five are observed. The spectral features due to the higher-energy intra-cationic  $d$ - $d$  transitions are obscured by intense absorption due to the  $O^{2-} \rightarrow Fe^{3+}$  charge-transfer process (Figs. 3 and 4). The spectra of Fig. 3 (specimen 1) show a number of weak features, which because of their intensity, number and energy can be ascribed, with a fair degree of certainty, to  $d$ - $d$  transitions of octahedrally coordinated  $Fe^{3+}$ .

The doubly degenerate, field independent,  ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$  transition is known to occur in the 21000 to 23000  $cm^{-1}$  range, for example, in muscovite (Faye, 1968*a*), andradite and vesuvianite (Manning, 1967, 1968*a*) and epidote (Burns and Strens, 1967). Therefore, it is reasonable to assign the 23100 and 22100  $cm^{-1}$  shoulders in the andalusite spectra of Fig. 3 to this transition, and, to assume that the degeneracy has been lifted by a modest distortion of the  $Fe^{3+}$  site from  $O_h$  symmetry. It also follows that the narrowly split shoulders at 25200 and 24600  $cm^{-1}$  in the  $E||a$  spectrum are probably low-symmetry components of the  ${}^6A_1 \rightarrow {}^4T_2(D)$

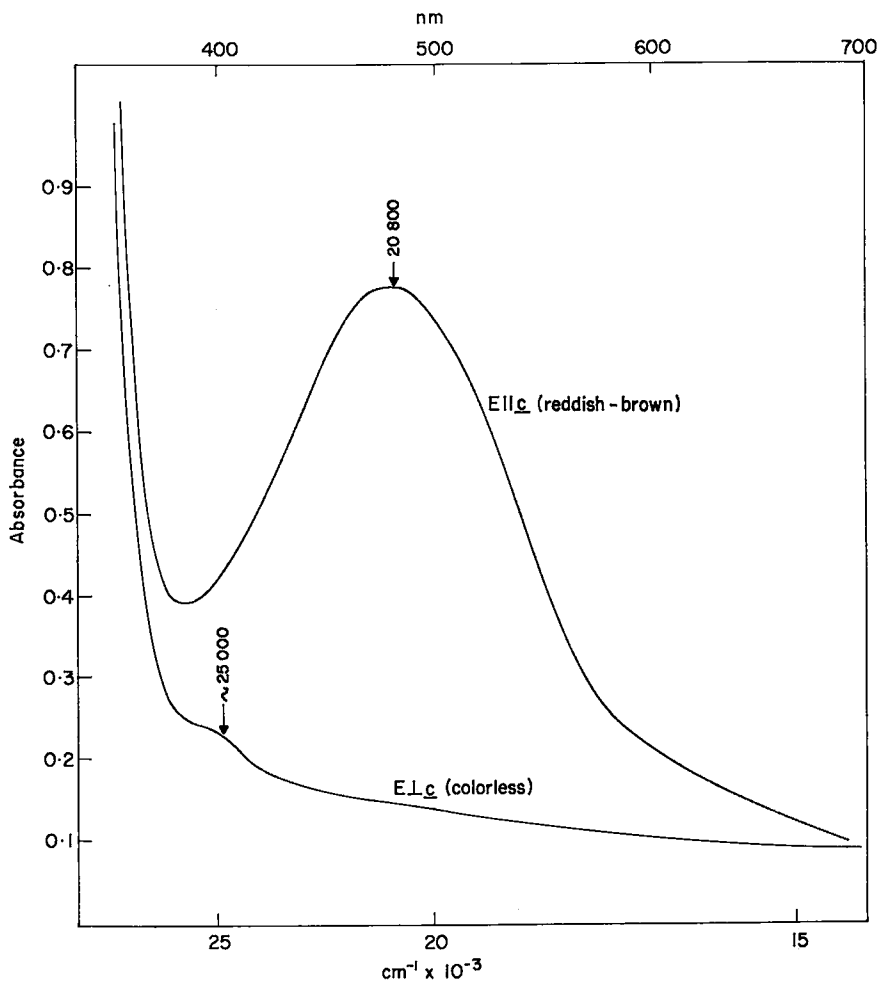


FIG. 4. Polarized spectra of andalusite in section 7 containing the  $c$ -axis, 0.1 cm thick.

transition. The broad diffuse shoulders centered near  $14500\text{ cm}^{-1}$  in the spectra of Fig. 3 are probably due to one or both of the  ${}^6A_1 \rightarrow {}^4T_{1g}(G)$  and  ${}^6A_1 \rightarrow {}^4T_{2g}(G)$  transitions.

From Fig. 3 it is apparent that the yellow-green colour exhibited by the  $E||b$  spectrum of andalusite is mainly the result of relatively more intense u.v.-centered background absorbance than in the  $E||a$  spectrum. As mentioned previously this is considered to be due mainly to the  $O^{2-} \rightarrow Fe^{3+}$  charge-transfer process.

To account for the variation in intensity of the u.v. charge-transfer

band it is rewarding to consider in detail the orientation and constitution of the (Al, Fe<sup>3+</sup>)-bearing octahedra in Figs. 1 and 2. The oxygen anions to which the six-coordinated cations are bonded are not equivalent: two of these, the O<sub>a</sub> oxygen ions of Burnham and Buerger (1961) (Fig. 2), are at a somewhat greater distance, and are shared by a five-coordinated Al and by a Si ion. Thus it may be argued that the O<sub>a</sub> oxygen ions are less efficient in donating electronic charge to Fe<sup>3+</sup> ions than are the other four oxygen ions. Because the projections in the *a*-*b* plane of the four Fe-O<sub>a,b</sub> bonds are at an angle of ~30° to *b* and ~60° to *a*, it is understandable that the background charge-transfer absorption should be greater in E||*b* than in the E||*a* spectrum.

It is to be noted that relatively thin *a*-*b* sections, or such sections containing substantially less Fe than specimen 1, would not likely exhibit visible pleochroism because in their spectra the low-energy wing of the O<sup>2-</sup> → Fe<sup>3+</sup> charge-transfer band would have lower intensity and thus result in a lack of colour (*e.g.*, spectra of Fig. 3).

(b) *Strong Pleochroism of Sections Containing the c-Axis*

Figure 4 shows that in the visible region the E ⊥ *c* spectrum is featureless except for the shoulder at approximately 25000 cm<sup>-1</sup> and hence the andalusite section is essentially colourless. This spectrum, of course, is analogous to a combination of E||*a* and E||*b* spectra of Fig. 3; however, because of the thinness of the section and its relatively low iron content, it does not exhibit the details of the *d*-*d* spectrum of Fe<sup>3+</sup>.

The E||*c* spectrum is dominated by an intense broad band with a maximum at 20800 cm<sup>-1</sup>. In the band, blue and green light are absorbed strongly and the mineral section therefore has a reddish-brown colour. In thick sections the colour due to the E||*c* spectrum is black because the 20800 cm<sup>-1</sup> band is sufficiently broad and intense to cover the visible region (~400-700 mμ).

The Brazilian andalusite contains as impurities only Fe and Ti in appreciable concentration (Table 1). The 20800 cm<sup>-1</sup> band cannot be rationalized however, on the basis of intra-cationic *d*-*d* bands due to likely ions of these elements, *i.e.*, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Ti<sup>3+</sup> and Ti<sup>4+</sup>, in the octahedral sites.

From previous discussions, the spectrum of Fe<sup>3+</sup> can be dismissed as the source of the polarized band. Similarly, Fe<sup>2+</sup> can be eliminated because it is well known that the spin-allowed <sup>5</sup>T<sub>2</sub> → <sup>5</sup>E(D) transition for this ion in an octahedral array of oxygen occurs at approximately 10000 cm<sup>-1</sup> (*e.g.*, Faye, 1968). Further, Ti<sup>4+</sup> cannot be responsible for the 20800 cm<sup>-1</sup> band for it is a *d*<sup>0</sup> ion and cannot give rise to *d*-*d* transitions. However, Ti<sup>3+</sup>, a *d*<sup>1</sup> ion, exhibits an absorption band, due to spin-allowed

${}^2T_2 \rightarrow {}^2E(D)$  transition, at  $\sim 20000\text{ cm}^{-1}$  in  $\text{Ti}(\text{OH}_2)_6^{3+}$  (Hartmann and Schlafer, 1951),  $\sim 19000\text{ cm}^{-1}$  in  $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$  (McClure, 1962),  $19000\text{ cm}^{-1}$  in andradite (Manning 1967) and  $17200\text{ cm}^{-1}$  in chloritoid (Faye, Manning and Nickel, 1968). The extinction coefficient,  $\epsilon$ , for such bands is in the range 5–20 litre/mole·cm and this is typical of intra-cationic  $d-d$  bands in general. However, the  $\epsilon_{T1}$  values for the  $20800\text{ cm}^{-1}$  band in the  $E\parallel c$  spectra of sections 2–7 (Table 1) are, generally, at least an order of magnitude larger. On this basis then, the band cannot be attributed to  $\text{Ti}^{3+}$  alone. A further argument against the band being a  $d-d$  transition is the fact that it is completely polarized with respect to the  $c$ -axis. It would be expected that the  ${}^2T \rightarrow {}^2E(D)$  transition of  $\text{Ti}^{3+}$  in the moderately distorted octahedral sites of andalusite would have measurable intensity in the  $E \perp c$  spectrum and this is observed not to be the case.

The intensity and polarization properties of the band at  $20800\text{ cm}^{-1}$  are strongly reminiscent of those due to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  electron transfer in the spectra of a number of iron-bearing minerals (Littler and Williams, 1965; Faye, 1968; Faye, Manning and Nickel, 1968; Robbins and Strens, 1968). For such materials the bands are found in the energy range  $13500\text{--}17000\text{ cm}^{-1}$ . They have their maximum intensity when the vibration direction of polarized light is coincident with the direction along which there is possible overlap of  $t_{2g}$  orbital-lobes on adjacent Fe ions which share octahedral edges.

Fig. 2 shows that in andalusite the overlap of  $t_{2g}$  orbital lobes of transition-metal ions could certainly occur (Al–Al distances are 2.69 and 2.87 Å) in the  $c$ -direction, therefore it is reasonable to propose that the  $20800\text{ cm}^{-1}$  band in the  $E\parallel c$  spectrum is due to a photochemical charge-transfer process involving transition-metal ions in the octahedral sites of this mineral.

On the basis of its energy, the band at  $20800\text{ cm}^{-1}$  is unlikely to be due to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge transfer. This conclusion is supported by the lack of spectral features at  $\sim 10000\text{ cm}^{-1}$  that could be attributed to  $\text{Fe}^{2+}$ . Many ferromagnesian minerals whose spectra show a  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  interaction band also exhibit distinct bands or shoulders due to octahedral  $\text{Fe}^{2+}$ , and indeed, the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is usually  $>1$  (Faye, 1968; Faye, Manning and Nickel, 1968).

Because Fe ions cannot account for the band at  $20800\text{ cm}^{-1}$  it is reasonable to consider the possibility of  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  charge transfer. Indeed, the electronic interaction of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  has been found responsible for a band at  $21000\text{ cm}^{-1}$  in the spectrum of  $\text{Ti}(\text{IV}) \cdot \text{Ti}(\text{III})\text{Cl}_2$  in concentrated HCl solution (Jorgensen, 1957) and for a pleochroic band at  $22000$  and  $23000\text{ cm}^{-1}$  in the spectrum of clintonite and astro-



phyllite respectively (Manning, 1968*b*), and, also for a similar band at 22000  $\text{cm}^{-1}$  in the spectrum of brown tourmalines (Manning, 1968*c*). Thus, on the basis of similarity of energy, there seems to be ample justification for assigning the 20800  $\text{cm}^{-1}$  band of the  $E\parallel c$  spectrum of andalusite to  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  electron transfer. Such an assignment implies that some titanium be present as  $\text{Ti}^{3+}$ . However, except for some asymmetry in the 18000–20000  $\text{cm}^{-1}$  range, there is no good evidence for the  ${}^2T_2 \rightarrow {}^2E(D)$  transition of  $\text{Ti}^{3+}$  in the spectra of Figs. 3 and 4, or in unpolarized spectra of andalusite sections. This may be the result of a combination of low  $\epsilon$ -value ( $\leq \sim 10$  litre/mole·cm), and "swamping" by  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  charge-transfer absorption (*e.g.*, Fig. 3) or by the  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  feature (Fig. 4). The  ${}^2T \rightarrow {}^2E(D)$  band of  $\text{Ti}^{3+}$  tends to be broad and diffuse relative to the high-energy peaks of  $\text{Fe}^{3+}$  and thus could be more readily obscured by background absorbance.

Table 1 shows that the high  $\epsilon_{T_1}$  values for the 20800  $\text{cm}^{-1}$  band are associated with sections 1 and 2 which contain a relatively high concentration of Mg. This suggests the possibility that the presence of  $\text{Mg}^{2+}$  is conducive to the existence of  $\text{Ti}^{4+}$ , the acceptor ion in the  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  charge-transfer process, and, together these two ions maintain electro-neutrality in the lattice.

That the  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  interaction band is found at appreciably lower energy (20800  $\text{cm}^{-1}$ ) in the  $E\parallel c$  spectrum of andalusite than in corresponding spectra of clintonite, astrophyllite and brown tourmalines (22000–23000  $\text{cm}^{-1}$ ) is probably due to the fact that  $\text{Ti}^{3+}$ – $\text{Ti}^{4+}$  distances in andalusite are shorter than in the other minerals.

### SUMMARY

Results of this work indicate that the principal source of pleochroism is  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  charge transfer between ions located in the chains of octahedra that extend along the  $c$ -axis. Such a process involves the overlapping of  $t_{2g}$  orbital lobes of adjacent ions across octahedral edges and is stimulated when the vibration direction of polarized light is coincident with the  $c$ -axis. It is also proposed that the minor pleochroism of  $a$ - $b$  sections is due to the variation in  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  charge transfer with the vibration direction of the radiation field.

### ACKNOWLEDGEMENTS

The authors wish to thank P. O'Donovan for assistance in preparing the andalusite sections, and R. Craig for chemical analyses.

## REFERENCES

- BIL'DYUKEVICH, A. L., *et al.* (1960): Paramagnetic resonance in certain minerals. *Zh. Exsp. Teoret. Fiz.* **39**, 1548-1551.
- BURNHAM, C. W. & BUERGER, M. J. (1961): Refinement of the crystal structure of andalusite. *Z. Kristallogr.* **115**, 269-290.
- BURNS, R. G. & STRENS, R. G. J. (1967): Structural interpretation of polarized absorption spectra of the Al-Fe-Mn-Cr epidotes. *Mineral. Mag.* **36**, 204-226.
- BRAGG, L. & CLARINGBULL, G. F. (1965): Crystal structures of minerals. *The Crystalline State* **4**, 193. G. Bell and Sons, London.
- FAYE, G. H. (1968): 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.
- (1968a): The optical absorption spectra of certain transition metal ions in muscovite, lepidolite, and fuchsite. *Can. J. Earth Sci.* **5**, 31-38.
- 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. *Am. Mineral.* **53**, 1174-1201.
- HARTMANN, H. & SCHLAFFER, H. L. (1951): Light absorption of complex compounds of Ti(III). *Z. Physik. Chem. (Leipzig)* **197**, 116-142.
- HOLUJ, F., THYER, J. R. & HEDGECOCK, N. E. (1966): ESR spectra of Fe<sup>+8</sup> in single crystals of andalusite. *Can. J. Phys.* **44**, 509-523.
- JORGENSEN, C. K. (1957): Comparative ligand field studies. *Acta. Chem. Scand.* **11**, 73-85.
- LITTLER, J. G. F. & WILLIAMS, R. J. P. (1965): Electrical and optical properties of crocidolite and some other iron compounds. *J. Chem. Soc.*, 6368-6371.
- MANNING, P. G. (1967): Optical absorption spectra of some andradites and the identification of the <sup>6</sup>A<sub>1</sub> → <sup>4</sup>A<sub>1</sub> <sup>4</sup>E(G) transition in octahedrally bonded Fe<sup>3+</sup>. *Can. J. Earth Sci.* **4**, 3039-1047.
- (1968a): Optical absorption spectra of octahedrally bonded Fe<sup>3+</sup> in vesuvianite. *Can. J. Earth Sci.* **5**, 89-92.
- (1968b): On the origin of colour and pleochroism of astrophyllite and brown clintonite. *Can. Mineral.* **9**, 663-667.
- (1968c): An optical absorption study of the origin of colour and pleochroism in pink and brown tourmalines. *Can. Mineral.* **9**, 678-690.
- MCCLURE, D. S. (1962): Optical spectra of transition-metal ions in corundum. *J. Chem. Phys.* **36**, 2757-2779.
- ROBBINS, D. W. & STRENS, R. G. J. (1968): Polarization-dependence and oscillator strengths of metal-metal charge-transfer bands in ions (II, III) silicate minerals. *Chem. Comm.*, 508-509.
- WHITE, E. W. & WHITE, W. B. (1967): Electron microprobe and optical absorption study of colored kyanites. *Science* **158**, 915-917.

*Manuscript received November 29, 1968, emended January 24, 1969*