ON THE ORIGIN OF COLOUR AND PLEOCHROISM OF KYANITE[1]

G. H. FAYE[2] AND E. H. NICKEL[3]

ABSTRACT

Although the colour and pleochroism of blue kyanite has been attributed to the presence of Ti^{3+} by previous workers, the present study of the polarized absorption spectra of such kyanite indicates that $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer accounts more readily for the optical properties. Experimental evidence is given for the presence of both Fe^{2+} and Fe^{3+} in blue kyanite and proposals are made for the manner in which these ions interact, across octahedral edges, to give rise to a pleochroic absorption band at 16500–17000 cm^{-1}. The direction of maximum intensity of this band correlates directly with the principal optical direction, Z, of kyanite.

INTRODUCTION

Recently it has been proposed that the colour and pleochroism of a specimen of andalusite (Al_2SiO_5) from Brazil is due mainly to a $Ti^{3+} \rightarrow Ti^{4+}$ charge-transfer process (Faye and Harris, 1969). The blue colour of the polymorph, kyanite, has also been attributed to the presence of traces of Ti^{3+} by White and White (1967). However, on the basis of a detailed examination of the polarized absorption spectra and of the analysis of selected specimens of kyanite in this laboratory, it seemed more likely that the blue colour and visible pleochroism of this mineral were due to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process, a phenomenon which strongly influences the optical properties of many other minerals (Faye, 1968*a*; Faye, Manning and Nickel, 1968; Manning and Nickel, 1969). That $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer may be associated with blue kyanite has been suggested recently by Robbins and Strens (1968), but they did not attempt to validate this speculation experimentally.

It is the purpose of this work then, to present spectral evidence for the presence of both Fe^{2+} and Fe^{3+} in blue kyanite as well as for the charge-transfer interaction of these ions, possibly across octahedral edges. Such interaction produces a pleochroic absorption band at 16500–17000 cm^{-1}, the maximum intensity of which coincides with the principal optical direction Z and is responsible for the variation in blue colour as the orientation of the specimen is varied in polarized light.

[1] Crown copyright reserved.

[2] Research Scientist, Inorganic Chemistry Sub-division, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

[3] Head, Mineralogical Section, Mineral Sciences Division, Mines Branch, Ottawa, Canada.

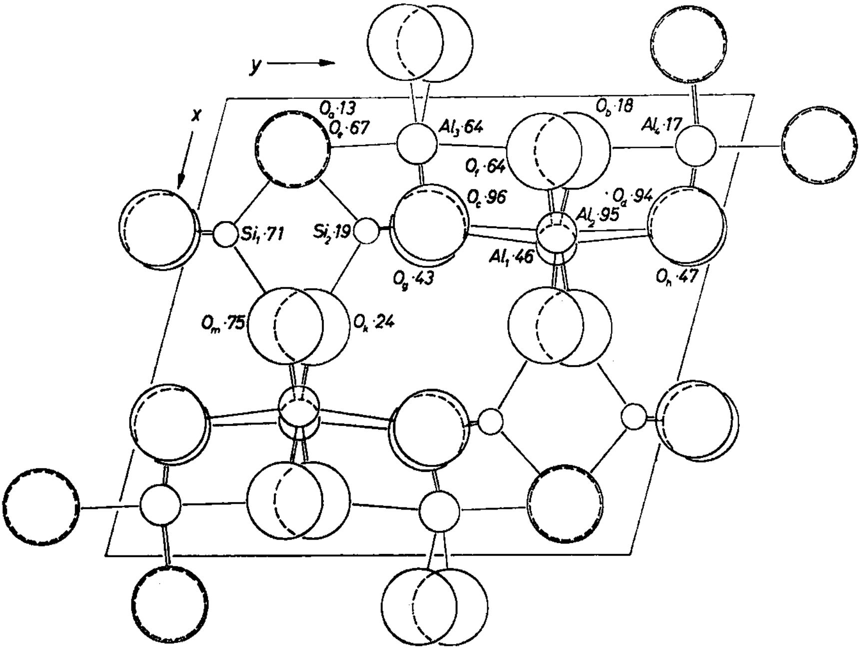

FIG. 1. The structure of kyanite as viewed along the *c*-axis, numbers indicating the *z*-coordinate of each atom. (after Burnham, 1963)

EXPERIMENTAL DETAILS

Preparation and Description of Kyanite Sections

One specimen of green, and two of blue, kyanite were investigated. The specimens were obtained through the courtesy of H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada. The localities of occurrence and partial analyses of these specimens are given in Table 1.

Although both the blue and green varieties of kyanite are zoned with respect to colour, the blue zones tend to be very thin layers parallel to (100), whereas the green zones are diffuse and more poorly defined. As Table 1 indicates, a specimen of the Brazilian kyanite was selectively cleaved to produce fractions varying in intensity of their blue colour and each of these was analysed for those transition metal ions that might be expected to influence its colour.

Oriented sections of the blue kyanites were obtained from mounted cleavage tablets by identifying the principal optical directions with a petrographic microscope and then cutting out the desired section with a tungsten-wire saw. The correct optical orientations of the completed

TABLE 1. PARTIAL ANALYSES AND LOCALITIES OF KYANITES

	Weight %			
	Fe	Ti	V	Cr
Blue, Minas Gerais, Brazil				
Pale blue fraction *a*	0.17 *	0.01	0.01	0.02
Medium blue ” *a*	0.15	0.01	0.01	0.03
Deep ” ” *a*	0.13	0.01	0.01	0.03
Deep ” ” *b*	0.17	N.D.	N.D.	N.D.
Unfractionated *b*	0.15	N.D.	N.D.	N.D.
Blue, Pizzo Forno, Switzerland				
Unfractionated *a*	0.17	0.01	0.01	<0.01
” *b*	0.18	0.02	N.D.	N.D.
Green, Avery County, N. Carolina				
Green Zone *b*	1.0–1.1	—	—	N.D.
Unfractionated *a*	0.35	N.D.	0.01	0.01
” *c*	0.24	—	N.D.	0.02

a—Semi-quantitative, emission spectrographic.
b—Electron microprobe (limit of detection for Ti ~ 0.01% (100 ppm)).
c—Chemical.
N.D.—not detected.
*The apparent inverse relationship between total Fe content and colour should not be significant because the analytical error is considered to be ±0.04%.

sections were verified by means of their optical interference figures before measurement of the spectra (Figs. 2, 3 and 5). Because green kyanite was found to be non-pleochroic, only its unpolarized spectrum was measured (Fig. 2).

Measurement of Spectra

All spectra were measured at room temperature with a Cary-14 recording 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 (Figs. 2 and 5) were calculated from $\epsilon = A/(C \times l)$, where A is the absorbance of the band maximum above background, 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 kyanite was 3.6 gram/ml.

DISCUSSION

Minor Elements in Kyanite

By scanning across a zoned blue kyanite with an electron microprobe, White and White (1967) correlated the titanium concentration (~10 to ~50 ppm) with the density of the blue colour. However, such a correlation does not seem possible from the analytical data of Table 1. For

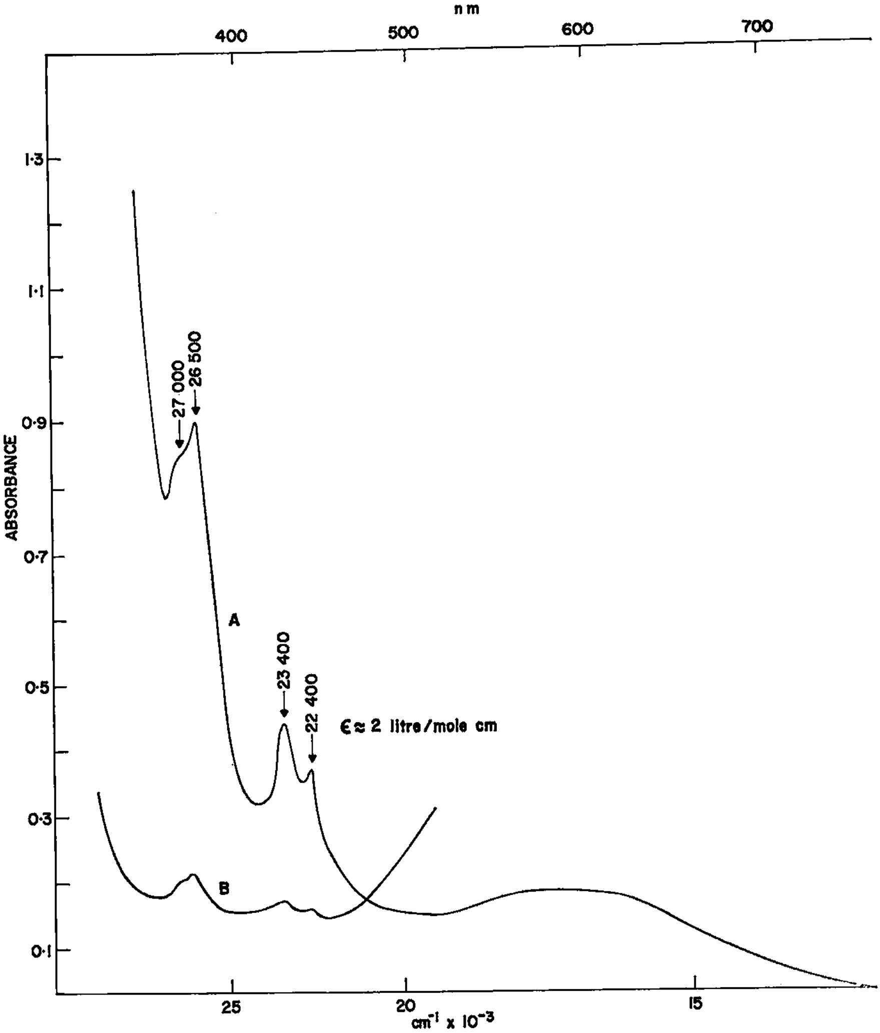

FIG. 2. A Unpolarized spectrum of green kyanite; thickness 0.30 cm.
B E||Z spectrum of blue kyanite (Brazil); thickness 0.28 cm.

example, it is seen that the distribution of the transition metals (total concentrations) is quite uniform in each of the fractions of the Brazilian kyanite which, relative to each other, vary widely in intensity of colour. Similarly, published analyses (*e.g.* Pearson and Shaw, 1960; Deer, Howie and Zussman, 1962; Herz and Dutra, 1964; Albee and Chodos, 1969) indicate that the blue colour of kyanite does not correlate well with titanium concentration.

However, it is to be noted that, in this laboratory, the limit of detection by electron probe for titanium is approximately 100 ppm. Therefore, the possibility that greater sensitivity of detection may have led to a correlation between titanium concentration and density of blue colour cannot be excluded.

Because there is no direct evidence in the present work, for an interpretation such as that of White and White (1967), an alternative proposal is made in which the colour and pleochroism of blue kyanite is attributed to iron, the only transition metal present in appreciable concentration. Such an approach is quite consistent with explanations made previously for the blue colour and pleochroism of cordierite and partially oxidized vivianite, (*e.g.* Faye, Manning and Nickel, 1968). The polarized spectra of these minerals reveal pleochroic absorption bands at ~17500 and 15500 cm^{-1} respectively, that were attributed to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process.

It remains then to show how this process can arise in blue kyanite.

The Structure of Kyanite

The crystal structure of kyanite, initially determined by St. Naray-Szabo *et al.* (1929), and subsequently refined by Burnham (1963), can be visualized as a distorted cubic close-packed array of oxygen atoms, with silicon occupying ten per cent of the tetrahedral interstices, and aluminium forty per cent of the octahedral interstices. (Strictly, these Al sites are non-centrosymmetric and distorted from O_h symmetry). The octahedral holes are filled in such a way that there is some sharing of edges between aluminium-centred octahedra. Fig. 1, taken from Burnham (1963), shows how this sharing of octahedral edges brings some of the aluminium ions relatively close together across the shared octahedral edges. This, as will be shown later, is of considerable significance in explaining the colour and pleochroism of kyanite. The distances between adjacent aluminium ions vary between 2.762 Å and 2.881 Å.

In an ideal close-packed cubic framework, there are six different vectors between the centres of adjacent octahedral sites. If the octahedral sites are unequally occupied, then there is a possibility that there may also be an inequality in the number of different vectors between the occupied sites. The vectors between adjacent aluminium sites in kyanite are plotted on a stereogram in Fig. 4, which shows that there the vectors are unequally distributed. The significance of this will become clear later.

Evidence for Fe^{3+} in Kyanite

Spectrum A of Fig. 2 is that of non-pleochroic green kyanite (Table 1). The prominent sharp features between 22000 and 27000 cm^{-1}, and

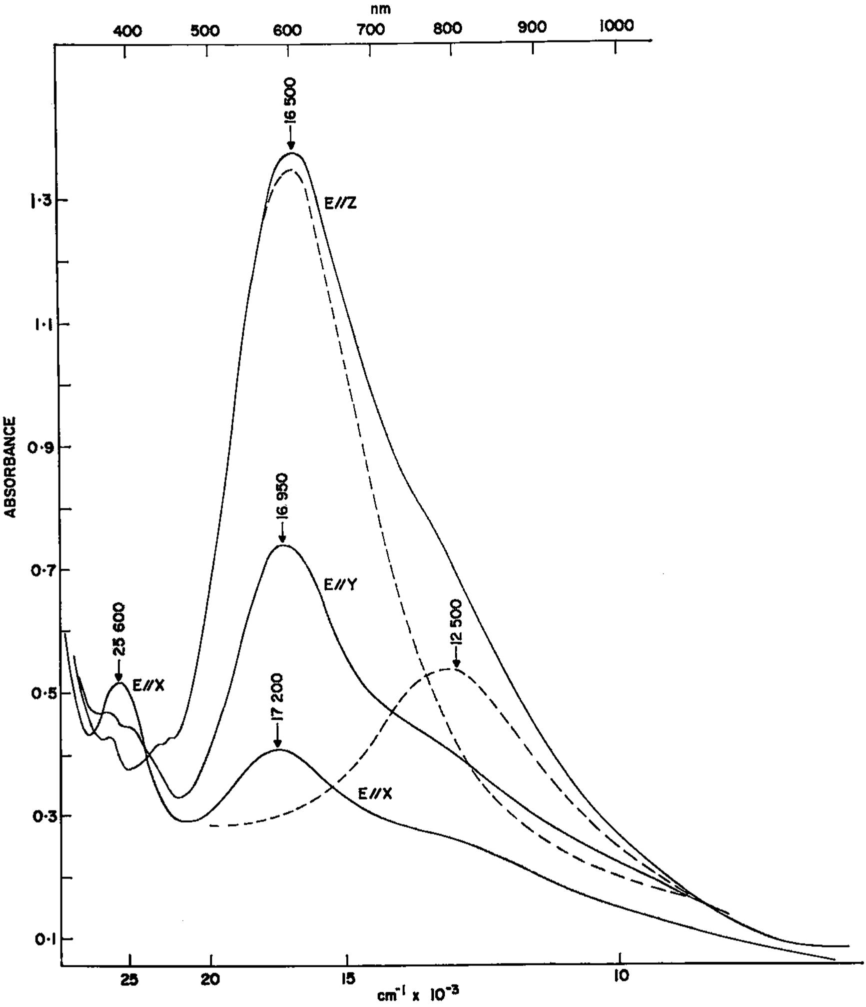

FIG. 3. Polarized spectra of blue kyanite (Brazil); thickness for E$\|$X spectrum 0.28 cm; thickness for E$\|$Y and E$\|$Z spectra 0.37 cm.

from 16000 to 17000 cm^{-1} are very similar in number and energy to those assigned to the low-intensity spin-forbidden transition of six-coordinate Fe^{3+} in andalusite (Faye and Harris, 1969). Paralleling such an assignment scheme, it follows that the bands at 26500 and 27000 cm^{-1} are due to the $^6A_1 \rightarrow {}^4T_2(D)$ transition, the pair at 22400 and 23400 cm^{-1} are due to the $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition, and the broad band centred between 16000 and 17000 cm^{-1} arises from one or both of the $^6A_1 \rightarrow {}^4T_1(G)$ and $\rightarrow {}^4T_2(G)$

transitions. The splitting within the two high-energy pairs of bands in the spectrum of andalusite was thought to be due to a modest distortion of the Fe^{3+} site from O_h symmetry (Faye and Harris, 1969). This is probably also true for kyanite; however in the kyanite lattice there are four kinds of six-coordinate sites (Fig. 1), so that the splitting in its spectrum may reflect the different geometries of these sites.

It is to be noted in passing that White and White (1967) reported a partial spectrum of a green kyanite that included a prominent band at 9300 cm^{-1}. This feature is not found in the spectrum of the green kyanite of this work but this may be because of its low intensity.

From Figs. 2 and 3 it is evident that the polarized spectra of the blue Brazilian kyanite also show, as minor bands, the features that are attributed to the spin-forbidden transitions of Fe^{3+} in green kyanite.

Evidence for Fe^{2+} in Blue Kyanite

If the major pleochroic band at $\sim$16500 to 17000 cm^{-1} in the spectra of Fig. 3 is to be ascribed to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process, then it is necessary to seek evidence for the presence of octahedrally co-ordinated Fe^{2+}.

This ion theoretically gives rise to a single absorption band due to the $^5T_2 \rightarrow {}^5E(D)$ transition. In an octahedral array of six oxygens this is found at approximately 10000 cm^{-1} in the spectrum of many minerals (*e.g.* Faye, 1968*a*; Faye, Manning and Nickel, 1968), whose average Fe^{2+}–O distances are $\sim$2.0 Å or greater. However, in the spectrum of golden beryl, whose Al^{3+} sites are not unlike those of kyanite, the $^5T_2 \rightarrow {}^5E(D)$ transition is found at 12500 cm^{-1} (Grum-Grzhimailo *et al*, 1962; Wood and Nassau, 1968). That the band is at higher energy in the spectrum of beryl is probably due to the relatively short Al–O distance of 1.94 Å (Bragg and West, 1924).

Thus it is suggested that the broad shoulder (resolved in the $E \| Z$ Spectrum by a Dupont Model 310 curve resolver) centred at $\sim$12500cm^{-1} in the spectra of Fig. 3 is also due to six co-ordinate Fe^{2+} in blue kyanite, (Al–O distances range from 1.90 to 1.93 Å).

The variation of intensity of the 12500 cm^{-1} band in the spectra of Fig. 3 is not well understood but may well be a function of the polarization dependence of the coupling (vibronic) of electronic and vibrational states (Cotton, 1963). It is to be noted that the 12500 cm^{-1} band of the beryl spectrum is also highly polarized (Wood and Nassau, 1968), as are the Fe^{2+} bands in tourmaline and cordierite (Faye, Manning and Nickel, 1968), for example.

From the $E \perp c$ spectrum of an analysed specimen of golden beryl, the authors have calculated the extinction coefficient, ϵ, of the 12500 cm^{-1}

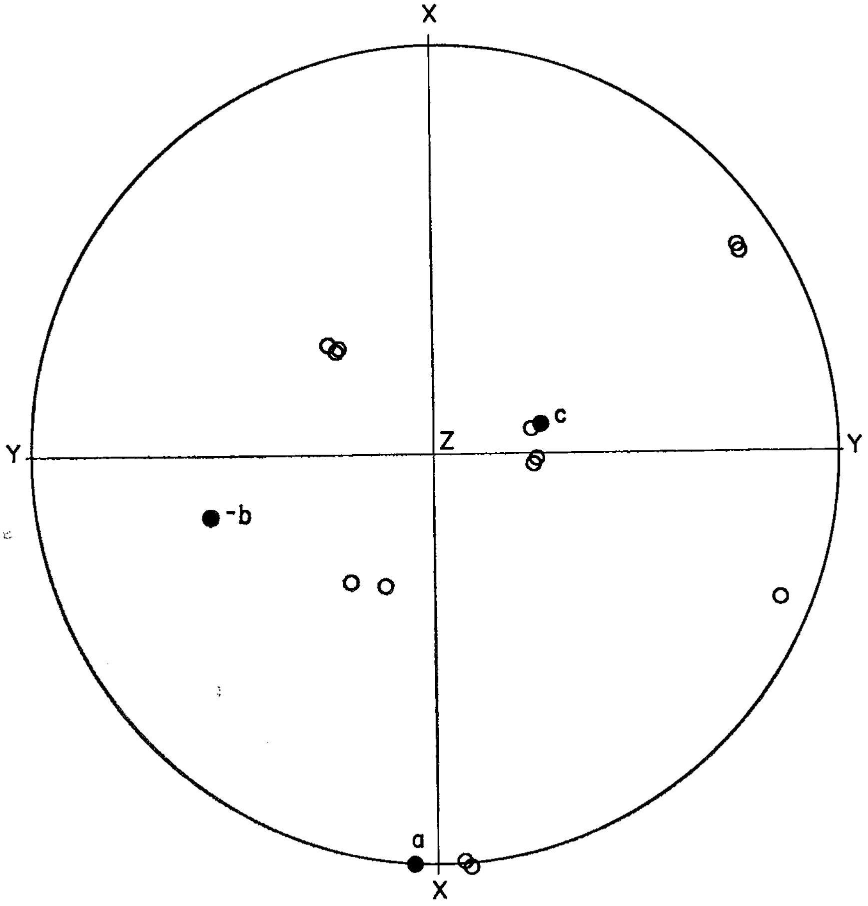

FIG. 4. Stereographic projection of the poles of the Al–Al vectors in kyanite, in relation to the principal optical directions (X, Y, Z) and the crystallographic axes (*a*, *−b*, *c*). All points are plotted on the upper hemisphere.

band to be ~25 litre/mole·cm. Assuming this value is appropriate for the E||Z spectrum of Brazilian kyanite, it can be estimated that its Fe^{2+} concentration is approximately 0.05%, or, approximately one-third of the total Fe content (Table 1).

$Fe^{2+} \rightarrow Fe^{3+}$ Charge-Transfer Band

From the foregoing there would seem to be justification for concluding that the major pleochroic band of blue kyanite is due to the same $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process previously found to influence the colour and pleochroism of other iron-bearing minerals (Faye, 1968*a*;

Faye, Manning and Nickel, 1968). The $Fe^{2+} \rightarrow Fe^{3+}$ bands in the spectra of these materials have their maximum intensities when the vibration direction is coincident with the direction along which there is possible overlap of t_{2g} orbital lobes on adjacent Fe ions which share octahedral edges.

A consideration of Fig. 1 indicates that there is abundant sharing of octahedral edges in kyanite; furthermore, the Al–Al distances are relatively short, varying from 2.76 to 2.88 Å. Therefore it is readily understandable that $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer could occur via overlapping t_{2g} orbital lobes. However, as shown in Fig. 4, there is more than one direction of orbital overlap (their directions coinciding with vectors joining occupied octahedral sites) and therefore the relationship between the direction of maximum absorption and that of *d*-orbital overlap is not so simple. Nevertheless, the majority of the vectors fall into three groups, and the centre of gravity of these three groups coincides closely with the Z optical direction. Since Z is the direction of maximum absorption in blue kyanite, it is reasonable to conclude that the absorption in this direction is due to charge transfer between iron atoms substituting for aluminium in the octahedral sites, and is the resultant of this process in three main directions.

Alternative schemes were considered, including possible orbital overlap directions between ions in normally occupied octahedral sites and those in the vacant octahedral sites, but the resultant distribution of vectors did not agree with the direction of maximum absorption. Consideration was also given to the implications of concentrating the iron atoms in only one of the four aluminium sites (Al_4, as suggested by Troup and Hutton (1964) on the basis of paramagnetic resonance studies). However, the vectors between adjacent Al_4 sites and those between Al_4 and vacant octahedral sites again could not be brought into agreement with the principal absorption direction. Consequently, if the close relationship between the direction of charge transfer via *d*-orbital overlap and the direction of maximum absorption observed in other minerals is valid for kyanite, then it must be concluded that the iron atoms in blue kynaite substitute for aluminium in all four octahedral sites, with no discernible site preference.

It was calculated previously that the Fe^{2+} concentration of the Brazilian kyanite is approximately 0.05%. If it is assumed, in the extreme, that every Fe^{2+} ion interacts with an adjacent Fe^{3+} ion, then the ϵ-value for the 16500 cm^{-1} band in the $E\|Z$ spectrum is calculated to be approximately 100 litre/mole·cm. This value is of the same order of magnitude as those calculated, on the same basis, for the molar extinction coefficient of the $Fe^{2+} \rightarrow Fe^{3+}$ band in the spectra of tourmaline and cordierite (Faye, Manning and Nickel, 1968), osumilite (Faye, unpublished) and riebeckite (Manning and Nickel, 1969).

It was noted above that the colour zones in the blue kyanite specimens of this work occur as very thin layers parallel to (100) and this strongly suggests the clustering of Fe^{2+} ions in these layers.

From the foregoing it can be concluded that the blue colour of kyanite should correlate directly with the presence of Fe^{2+} (and the corresponding Fe^{3+} ions as electron acceptors). As a consequence, it is suggested that when there is an apparent correlation between titanium concentration and blue colour, then titanium may be present as Ti^{4+} which acts in conjunction with Fe^{2+} to maintain electroneutrality in the kyanite lattice. However, based on values of 0.05% and 0.01%, there is no such correlation between Fe^{2+} and titanium respectively for the Brazilian kyanite of the present work.

Largely on the basis of electron probe analysis, White and White (1967) attributed the pleochroic 16670 cm^{-1} band of a blue Indian kyanite to traces of Ti^{3+}. These workers indicated that, because of the relatively low energy and high intensity (based on Ti concentration), it is difficult to assign the band to a simple *d–d* transition. Yet, beyond referring to a narrow *d* band, White and White did not specify the nature of the electronic transition giving rise to the spectral feature in question. Also, no attempt was made to explain the origin of the polarization properties (pleochroism) of the 16670 cm^{-1} band.

In view of these problems the present authors prefer the model based on the interaction of Fe^{2+} and Fe^{3+}.

Spectral Evidence for Cr^{3+} in Brazilian Kyanite

Spectrographic analyses (Table 1) indicate the presence of a significant concentration of Cr in the Brazilian kyanite. The $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions of Cr^{3+} in an octahedral environment of six oxygens in many silicate minerals are known to occur in the 16500–18000 cm^{-1} and 23000–26000 cm^{-1} ranges respectively (*e.g.* Faye, 1968*b*; Manning, 1969). Therefore, it is proposed that the 17200 cm^{-1} and 25600 cm^{-1} bands in spectrum A of Fig. 5 and in the $E\|X$ spectrum of Fig. 3 are those due to Cr^{3+} substituting for Al^{3+} in the Brazilian kyanite. The calculated ϵ-value of ~30 litre/mole·cm for the 25600 cm^{-1} feature is appropriate for Cr^{3+}. The absence of the well-defined high-energy band in the spectrum of the Swiss kyanite (B, Fig. 5) which does not contain a detectable amount of Cr, tends to confirm the above assignments. Barely discernible in the high-energy side of the 25600 cm^{-1} band of spectrum A are shoulders due to spin-forbidden transitions of Fe^{3+} (see Fig. 2).

Figs. 3 and 5 show that at least the 25600 cm^{-1} band of the Brazilian

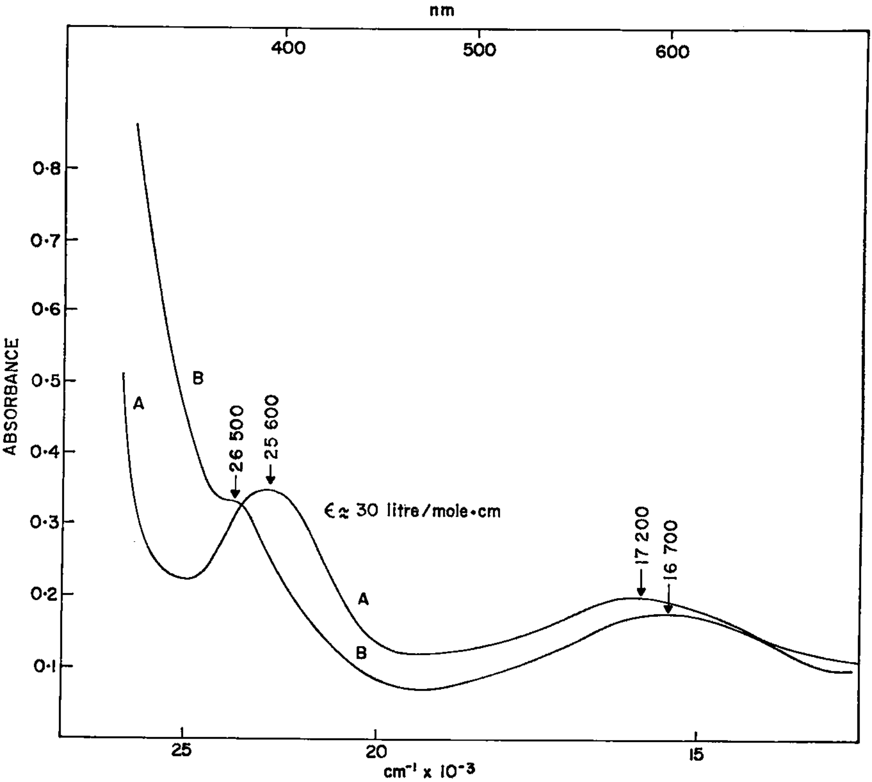

FIG. 5. A E||X spectrum of blue kyanite (Brazil), thickness 0.28 cm.
B E||X spectrum of blue kyanite (Switzerland), thickness 0.70 cm.

kyanite is highly polarized, apparently with intensity that is inversely proportional to that of the $Fe^{2+} \rightarrow Fe^{3+}$ band; however, no attempt was made to establish selection rules that could account for this.

It is to be noted from spectrum B of Fig. 5 that the $Fe^{2+} \rightarrow Fe^{3+}$ band at 16700 cm^{-1} has appreciable intensity in the E||X spectrum. Therefore, the 17200 cm^{-1} band of the E||X spectrum of the Brazilian kyanite in Fig. 3 is probably a composite of the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band and that due to the $^4A_2 \rightarrow {}^4T_1$ transition of Cr^{3+} in pseudo-octahedral sites.

ACKNOWLEDGEMENTS

The authors wish to thank D. C. Harris and P. E. Porteous for electron microprobe analyses, G. L. Mason for spectrographic analyses and R. R. Craig for chemical analyses. Thanks are also due to P. O'Donovan for assistance in the preparation of the mineral specimens.

REFERENCES

ALBEE, A. L. & CHODOS, A. A. (1969): Minor element content of coexistent Al_2SiO_5 polymorphs. *Amer. J. Sci.* **267**, 310–316.

BRAGG, W. L. & WEST, J. (1926): The structure of beryl, $Be_3Al_2Si_6O_{18}$. *Proc. Roy. Soc.* **A111**, 691–714.

BURNHAM, C. W. (1963). Refinement of the structure of kyanite. *Z. Kristallogr.* **118**, 337–360.

COTTON, F. A. (1963): *Chemical Applications of Group Theory.* Interscience Publishers, John Wiley and Sons, New York, p. 231.

DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals,* **1**. Longmans, Green and Co., London, p. 139.

FAYE, G. H. (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 spectra of certain transition metal ions in muscovite, lepidolite, and fuchsite. *Can. J. Earth Sciences,* **5**, 31–38.

FAYE, G. H. & HARRIS, D. C. (1969): On the origin of colour and pleochroism in andalusite from Brazil. *Can. Mineral.,* 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.

GRUM-GRZHIMAILO, S. V., BRILLIANTOV, N. A., SVIRIDOVA, R. K., SUKHANOVA, O. N. & KAPITONOVA, M. M. (1962): Absorption spectra of iron-colored beryls at temperatures from 290 to 1.7°K. *Optics Spectr.* **13**, 133–134.

HERZ, N. & DUTRA, C. V. (1964): Geochemistry of some kyanites from Brazil. *Amer. Mineral.* **49**, 1290–1305.

MANNING, P. G. (1969): Structural interpretations of the optical absorption spectra of chromium-bearing tourmaline, black tourmaline and buergerite. *Can. Mineral.,* in this issue.

MANNING, P. G. & NICKEL, E. H. (1969): A spectral study of the origin of colour and pleochroism of a titanaugite from Kaiserstuhl and of a riebeckite from St. Peter's Dome, Colorado. *Can. Mineral.,* in this issue.

PEARSON, G. R. & SHAW, D. M. (1960): Trace elements in kyanite, sillimanite and andalusite. *Amer. Mineral.* **45**, 808–817.

ROBBINS, D. W. & STRENS, R. G. (1968): Polarization-dependence and oscillator strengths of metal-metal charge-transfer bands in iron (II, III) silicate minerals. *Chem. Comm.* 508–509.

ST. NARAY-SZABO, TAYLOR, W. H. & JACKSON, W. W. (1929): The structure of kyanite. *Z. Kristallogr.* **71**, 119–130.

TROUP, G. J. & HUTTON, D. R. (1964): Paramagnetic resonance of Fe^{3+} in kyanite. *Brit. J. Appl. Phys.* **15**, 1493–1499.

WHITE, E. W. & WHITE, W. B. (1967): Electron microprobe and optical absorption study of colored kyanites. *Science,* **158**, 915–917.

WOOD, D. L. & NASSAU, K. (1968): The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *Amer. Mineral.* **53**, 777–800.

Manuscript received February 26, 1969, emended April 28, 1969