

# 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<sup>1</sup>

P. G. MANNING<sup>2</sup> AND E. H. NICKEL<sup>3</sup>

## ABSTRACT

A spectral study is reported of the origin of colour and pleochroism of a titanaugite from Kaiserstuhl, Germany. Polarised spectra of *a-b* sections of titanaugite show a pleochroic band at  $\sim 14000\text{ cm}^{-1}$  that has been assigned to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge-transfer. Intra-cationic *d-d* bands of octahedrally-bonded  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ti}^{3+}$  have been observed at  $10000\text{ cm}^{-1}$ ,  $22000\text{ cm}^{-1}$  and  $19000\text{ cm}^{-1}$ , respectively. Polarised spectra of *a-c* sections of riebeckite from St. Peter's Dome, El Paso County, Colorado, show a pleochroic band at  $15700\text{ cm}^{-1}$  that is polarised along metal-metal directions, and is assigned to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge-transfer. The field-independent transition  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1\text{E}(\text{G})$  in  $\text{Fe}^{3+}$  is observed at  $23000\text{ cm}^{-1}$ . Intra-cation *d-d* bands of  $\text{Fe}^{2+}$  appear as weak shoulders on the limb of the  $15700\text{ cm}^{-1}$  band.

## INTRODUCTION

That optical absorption spectrophotometry is a facile means of providing information on the structures of transition metal-bearing minerals is now well established. Optical spectra have been used to determine the local symmetry of the anionic environment around the cation (Burns, 1965; Burns and Strens, 1967). Other workers have studied minerals whose absorption spectra are complicated by the simultaneous presence of two or more transition metal ions, but in which site distortions from cubic symmetry are relatively unimportant in the spectral interpretations (Faye, 1968*a, b*; Manning, 1967*a, b*). In the latter type of study, information has been obtained on the location and valence states of transition metals in a variety of minerals, the analytical implications of which are worthy of further study.

In an electrostatic crystal field, the cation *3d* orbitals are split, and this splitting gives rise to a number of electronic energy levels. Electronic transitions from the ground state to higher energy levels occur by way of absorption of radiation in and around the visible region of the electromagnetic spectrum. Energy-level diagrams for transition metal ions in

<sup>1</sup>Crown copyright reserved.

<sup>2</sup>Research Scientist, Mineral Sciences Division, Department of Energy, Mines and Resources, Ottawa, Canada. Present address: Inland Waters Branch, No. 8 Temporary Bldg., Carling Ave., Ottawa, Ont.

<sup>3</sup>Head, Mineralogy Section, Mineral Sciences Division, Department of Energy, Mines and Resources, Ottawa, Canada.

cubic fields have been calculated by Tanabe and Sugano (1954), and the comparison of the observed absorption bands with these energy-level diagrams permits the assignment of the bands. It should be stressed that these transitions, which form the basis of the work described in the previous paragraph, occur between energy levels within a given transition-metal ion.

A recent development in the study of the absorption spectra of minerals has been the assignment of pleochroic bands, in the energy range  $13500\text{--}17000\text{ cm}^{-1}$  ( $750\text{--}600\text{ m}\mu$ ), to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  electron transfer. In 1965, Littler and Williams assigned a strong absorption in the spectrum of crocidolite to  $\text{Fe}^{2+}\text{--}\text{Fe}^{3+}$  interaction, and confirmed their assignment with electrical-conductivity measurements. Faye (1968*a, b*), Robbins and Strens (1968) and Faye, Manning and Nickel (1968) have identified  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge-transfer bands in tourmaline, sheet silicates, cordierite, kyanite and vivianite. Faye, Manning and Nickel (1968) estimated the extinction coefficients of the bands to be  $>100$ , while Robbins and Strens (1968) calculated extinction coefficients to be in the range  $150\text{--}1000$ , depending on the mineral. In these minerals, the Fe atoms share octahedral–octahedral or octahedral–tetrahedral edges, and electron exchange occurs by way of direct cation  $d$ -orbital overlap or by indirect overlap by way of oxygen  $p\pi$  orbitals.

However, comparatively little is known of the spectra of Ti-bearing minerals. Titanium has two main valence states,  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ , and the ions have different ionic radii ( $0.76$  and  $0.67\text{ \AA}$ ). Both are known to occur in silicate minerals, although, in general, one valence state will predominate in a given mineral.  $\text{Ti}^{4+}$ , being a  $3d^0$  ion, does not exhibit intra-cationic  $d\text{--}d$  bands, and for this reason  $\text{TiO}_2$  is a colourless pigment. However,  $\text{Ti}^{3+}$ , a  $3d^1$  ion, when in octahedral coordination, absorbs in the blue-green part of the spectrum; the absorption is relatively broad and marks the only spin-allowed transition  $t_{2g} \rightarrow e_g$ . The ion  $\text{Ti}^{3+}$  absorbs at  $19000\text{ cm}^{-1}$  in andradite (Manning, 1967*a*),  $17200\text{ cm}^{-1}$  in chloritoid (Faye, Manning and Nickel, 1968) and at  $20300\text{ cm}^{-1}$  in  $\text{Ti}(\text{OH})_6^{3+}$  (Hartmann and Schlafer, 1951). Apparently, therefore, a broad absorption band in the blue-green region of the spectrum of a Ti-bearing mineral identifies  $\text{Ti}^{3+}$ , while the additional presence of  $\text{Ti}^{4+}$  may in some instances be inferred from the extinction coefficient of the band (spin-allowed intra-cationic  $d\text{--}d$  bands generally have extinction coefficients of  $5\text{--}50$ ).

Manning has assigned absorption bands at  $22000\text{--}23000\text{ cm}^{-1}$  in the spectra of astrophyllite (1968*a*), brown clintonite (1968*a*) and brown tourmaline (1968*b*) to  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  charge transfer. The band in each mineral is pleochroic, and is polarized along the Ti–Ti directions, which

lie in the 001 planes of clintonite and tourmaline but are perpendicular to the 001 plane of astrophyllite. This accounts for the different pleochroic schemes of clintonite and astrophyllite, the former showing maximum absorption in  $E \parallel (001)$  spectra and the latter in  $E \perp (001)$  spectra.

In the current paper, the absorption spectra of a titanaugite from Kaiserstuhl are examined. The colour of titanaugite has earlier been assigned to  $Ti^{3+}$  (Burns and Fyfe, 1967), presumably because of the similarity of the spectrum to that of  $Ti(OH_2)_6^{3+}$ .

Polarized absorption spectra of a riebeckite from St. Peter's Dome, El Paso County, Colorado, are also reported in this work. Although the Prussian-blue colour of crocidolite has earlier been assigned to  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer (Littler and Williams, 1965), the polarization properties of the band are nevertheless of interest.

#### EXPERIMENTAL DETAILS

The titanaugite, reportedly from Limberg, Kaiserstuhl, Germany, was provided by R. Schaffrath, a private collector in Frankfurt, Germany. The sample consisted of black grains of titanaugite in limburgite. The riebeckite is from St. Peter's Dome, El Paso County, Colorado, and was provided by H. R. Steacy, curator of the Reference Series of the National Mineral Collection, Ottawa.

Oriented thin sections of both minerals were prepared by orienting single crystals by their external morphology, and cutting 1-mm thick slabs by means of a wire saw, polishing one side, and mounting it on a glass slide. The other side of the slab was ground and polished to the desired thickness. Orientations were confirmed by optical interference figures obtained by means of a petrographic microscope.

Because of the cleavage properties of riebeckite, it was not possible to prepare  $a$ - $b$  sections thin enough to permit resolution of the  $15700\text{-cm}^{-1}$  band in  $E \parallel b$  spectra. Accordingly,  $a$ - $c$  and  $b$ - $c$  sections were prepared, and  $E \perp c$  and  $E \parallel c$  spectra of an  $a$ - $c$  section are presented in this paper.

Spectra were measured with Cary-14 or Beckman DK-2A double-beam spectrophotometers. Nicol prisms were used with the former instrument and Polaroid film with the latter, as polarizers.

Extinction coefficients are calculated from

$$\epsilon = \frac{A}{C \times l} \text{ litre/mole} \cdot \text{cm}$$

where  $A$  is the band absorbance,  $C$  is the cation concentration in moles/litre and  $l$  is the thickness (in cm) of the sample.

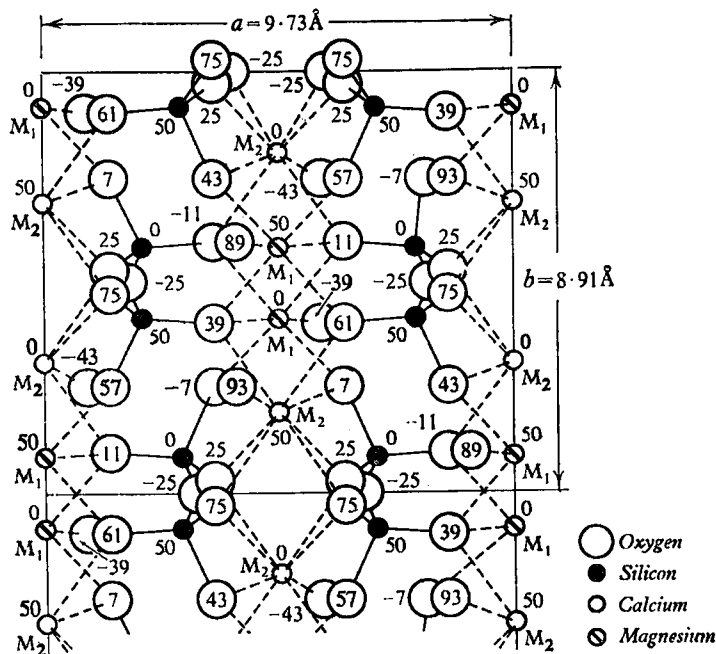


FIG. 1. Structure of diopside projected on 001 (from Warren and Bragg, 1928); this can be taken as an approximation of the titanaugite structure.

## DISCUSSION

### *Structures of titanaugite and riebeckite*

The structure of titanaugite,  $\text{Ca}(\text{Mg, Fe, Ti})(\text{SiO}_3)_2$ , is generally regarded as being similar to that of diopside,  $\text{CaMg}(\text{SiO}_3)_2$ , which is presented in idealized fashion in Fig. 1. It is evident from Fig. 1 that, in an  $a$ - $b$  section, metal-metal interaction can occur by way of orbital overlap parallel to  $b$ , because of the sharing of octahedral edges in this direction. However, there will be no metal-metal charge transfer perpendicular to  $b$ . Therefore, polarized spectra of  $a$ - $b$  sections of titanaugite will allow the identification of metal-metal charge-transfer bands: such bands will be observed in  $E \parallel b(Y)$  spectra but not in  $E \parallel a(X + Z)$  spectra. ( $E$  represents the vibration direction of the electric vector of incident light.)

Considerations of ionic radii (Day and Selbin, 1962) alone suggest that the cations  $\text{Fe}^{2+}$  (0.76 Å),  $\text{Fe}^{3+}$  (0.64 Å),  $\text{Ti}^{3+}$  (0.76 Å) and  $\text{Ti}^{4+}$  (0.68 Å) will occupy the Mg (0.65 Å) sites ( $M_1$ ) predominantly, rather than the larger Ca (0.99 Å) sites ( $M_2$ ). This reasoning is supported by

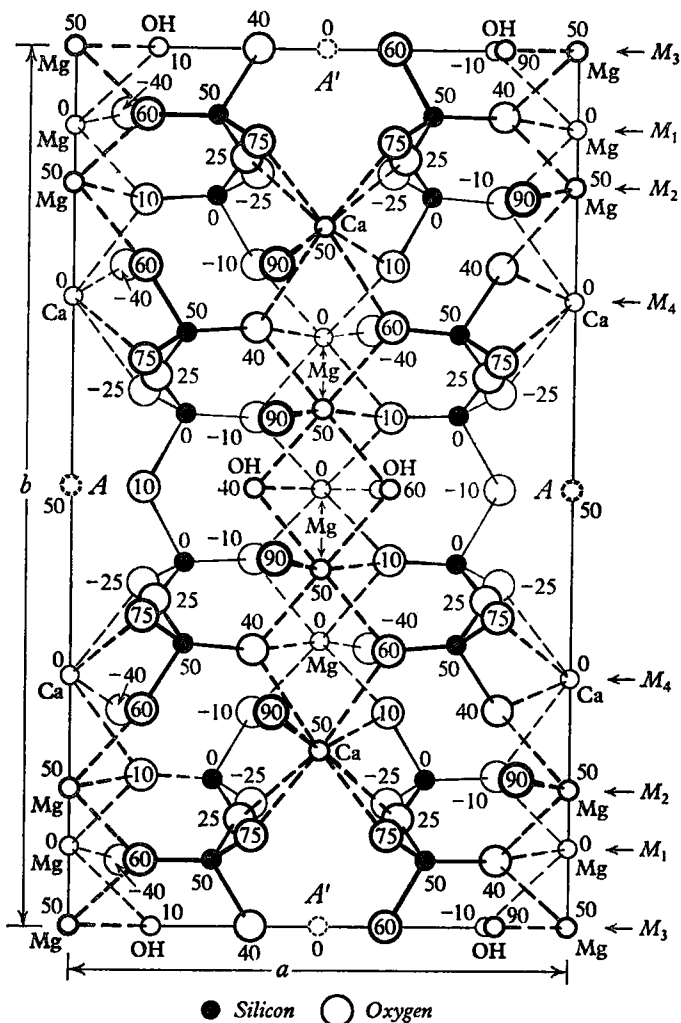


FIG. 2. Structure of tremolite projected on 001 (from Bragg, 1937); this can be taken as an approximation of the riebeckite structure.

the fact that a continuous range of compositions exists between the extremes of diopside,  $\text{CaMg}(\text{SiO}_3)_2$ , and hedenbergite,  $\text{CaFe}(\text{SiO}_3)_2$ .

The structure of riebeckite,  $\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}(\text{Si}_8\text{O}_{22})(\text{OH}, \text{F})_2$ , is similar to that of tremolite, which is presented diagrammatically in Fig. 2. Here, also, metal-metal charge transfer can occur when the vibration direction ( $E$ ) of the electric vector of incident light is parallel to  $b$ , but not when  $E \parallel a$  because  $E$  is then perpendicular to all metal-metal directions.

There are two Fe-Fe distances in riebeckite, 3.2 Å for  $M_2$ - $M_3$  and 3.1 Å for  $M_1$ - $M_2$  (Whittaker, 1949). It can be deduced from Fig. 2 that metal-metal charge-transfer bands will be observed in  $E||c$  spectra because the projection of the Fe-Fe distance onto the  $c$ -axis is large.

According to Whittaker (1949) and Burns and Prentice (1968), the  $Fe^{2+}$  and  $Fe^{3+}$  ions are non-randomly distributed over the  $M_1$ ,  $M_2$  and  $M_3$  sites in crocidolite. Most of the  $Fe^{3+}$  is located in the  $M_2$  sites, while  $Fe^{2+}$  ions predominate in the  $M_1$  and  $M_3$  positions with a preference for the former. A similar distribution can be assumed in riebeckite.

### *Spectra of riebeckite*

The  $E \perp c$  and  $E||c$  spectra of an  $a$ - $c$  section of riebeckite are shown in Fig. 3, from which it is evident why riebeckite is brown in the former orientation and Prussian blue in the latter. The  $E||a'$  ( $a'$  is the direction normal to  $b$  and  $c$ ) spectrum of an  $a'$ - $b$  section ( $\perp c$ ) is similar to the  $E \perp c$  spectrum of the  $a$ - $c$  section (Fig. 3), while  $E||c$  and  $E||b$  spectra are also qualitatively similar to each other.

The Fe concentrations in our sample of riebeckite are approximately 10% lower than the Fe values determined by Kunitz (1930) on a riebeckite from Pike's Peak. Our riebeckite, therefore, has 1.7  $Fe^{3+}$  and 2.4  $Fe^{2+}$  ions per unit formula, compared with 2 and 3 ideally. The pleochroic properties of the 15700  $cm^{-1}$  band in  $E||a$  and  $E||c$  spectra (Fig. 3) show, in conjunction with the chemical analyses, that the band is an  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer band, confirming the conclusion of Littler and Williams (1965) for crocidolite. The energy of the band is in the middle of the range observed for  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer bands in other minerals (Robbins and Strens, 1968; Faye, Manning and Nickel, 1968). The  $\epsilon$ -value of the band is  $\sim 150$ , based on the  $Fe^{2+}$  concentration and on the number of  $Fe^{3+}$  neighbours per  $Fe^{2+}$  ion, and the thickness of the section.

The sharp absorption at 23000  $cm^{-1}$  in  $E||c$  spectra of riebeckite (Fig. 3) very likely marks the first field-independent transition  ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$  in  $Fe^{3+}$ . The band is sharp and prominent in  $E||b$  spectra also, but is weaker and less evident in  $E||a'$  spectra. In general, the intensity of the 23000  $cm^{-1}$  band follows the intensity of the 15700  $cm^{-1}$  charge-transfer band, and is probably a manifestation of Engleman (1960) mixing. The  $\epsilon$ -value of the 23000  $cm^{-1}$  band in  $E||c$  spectra is 10, confirming that, because spin-forbidden transitions have generally much lower values of  $\epsilon$  (Manning, 1967*a*), the band is "borrowing" intensity from the 15700  $cm^{-1}$  band.

The presence of only one sharp absorption band in the spectrum of riebeckite is consistent with earlier suggestions (Whittaker, 1949;

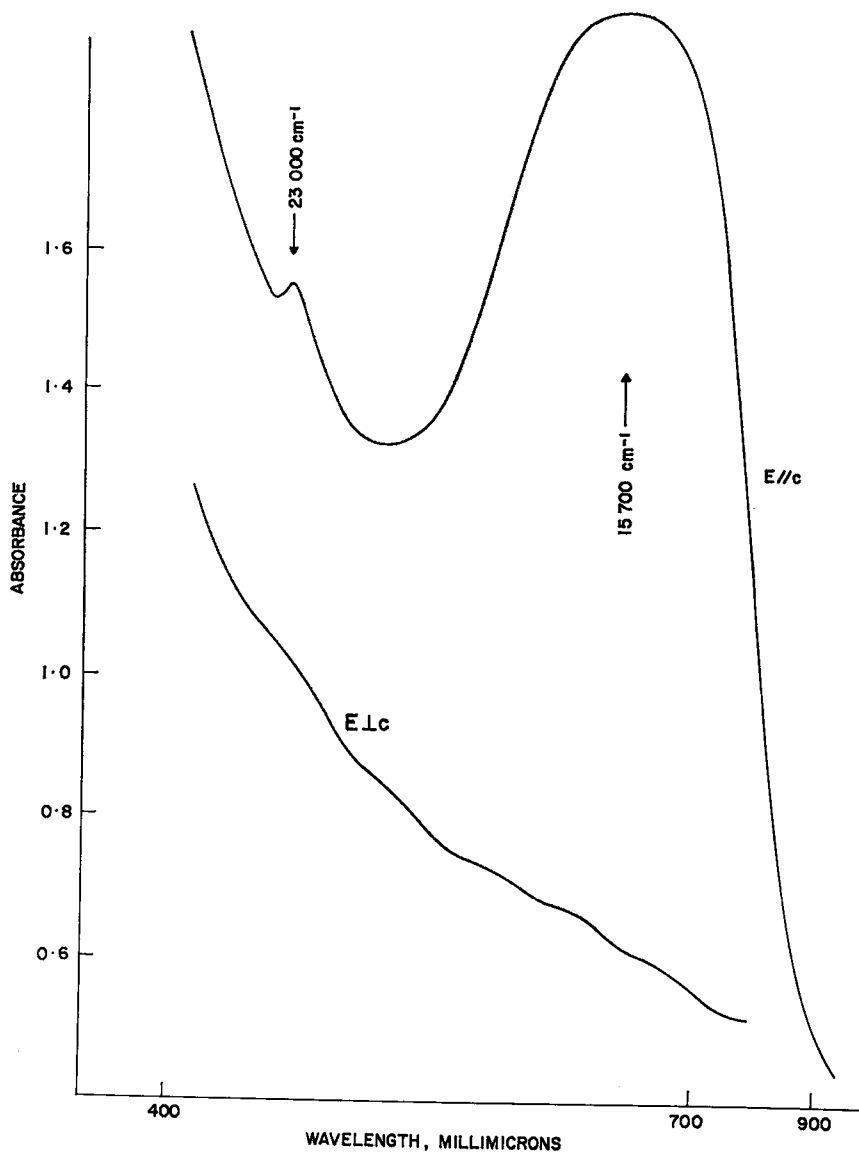


FIG. 3. Absorption spectra of an *a-c* (010) section of riebeckite, 0.02 mm thick.

Burns and Prentice, 1968) that  $\text{Fe}^{3+}$  ions are located mainly in one site.

The  $\text{Fe}^{2+}$  intra-cation  $d-d$  bands (not included in Fig. 3) occur as shoulders on the limb of the  $15700\text{ cm}^{-1}$  band. This, together with the fact that  $\text{Fe}^{2+}$  is distributed over  $M_1$ ,  $M_2$  and  $M_3$  sites makes interpretation of the bands difficult. The  $\text{Fe}^{2+}$   $d-d$  bands do not make important contributions to the colour and pleochroism of riebeckite, and so they will not be considered further here.

### *Spectra of titanaugite*

Polarized spectra of an  $a-b$  (001) section of titanaugite are shown in Fig. 4, while Fig. 5 shows the spectrum of a cleavage section in unpolarized light.

The interpretation of a spectrum depends, of course, on the clear-cut resolution of the bands that make up the absorption envelope. The spectra of titanaugite in Figs. 4 and 5 quite obviously have at least three components, two readily identifiable bands at  $10000\text{ cm}^{-1}$  and  $22000\text{ cm}^{-1}$  and also a very broad absorption that sweeps through most of the visible region. That this latter broad band is a composite of at least two other broad bands can be deduced in the following manner: firstly, the band, if centred around  $17000\text{ cm}^{-1}$ , would have a half-width of at least  $6500\text{ cm}^{-1}$ , which is too large for transitions of the type we are considering here; and secondly, in the  $600\text{ m}\mu$  region, the  $E\parallel a$  and  $E\parallel b$  spectra are concave and convex respectively, strongly suggesting that a broad band centred at approximately  $14100\text{--}15000\text{ cm}^{-1}$  is present in  $E\parallel b$  spectra but not in  $E\parallel a$  spectra. Intuitively, there has to be another broad absorption at  $\sim 19000\text{ cm}^{-1}$ . This interpretation is confirmed by the resolution of the spectra into their composites using a Dupont curve analyser. The number of composites derived from the envelopes depends on how the background charge-transfer band, centred in the ultraviolet region, sweeps into the visible region. The best fit was obtained assuming a skewed Gaussian shape for the absorption edge, resulting in the dashed curve in Fig. 5. The spectra in Fig. 4 were analysed using a similar background, which almost coincided with the spectral curve at approximately  $650\text{ m}\mu$  in  $E\parallel a$  spectra.

The unpolarized light spectra in Figs. 4 and 5 were resolved into four component bands, the bands having similar energies and shapes in both spectra. Judging by eye, as done above, the presence of four bands seems very reasonable. The component bands are shown in Fig. 5. The  $14000\text{ cm}^{-1}$  band in Fig. 4 is obviously pleochroic and accounts mainly for the pleochroism of the titanaugite. The  $10000\text{ cm}^{-1}$  and  $22000\text{ cm}^{-1}$  bands are only weakly pleochroic, and are likely therefore to be intra-cation  $d-d$  bands.



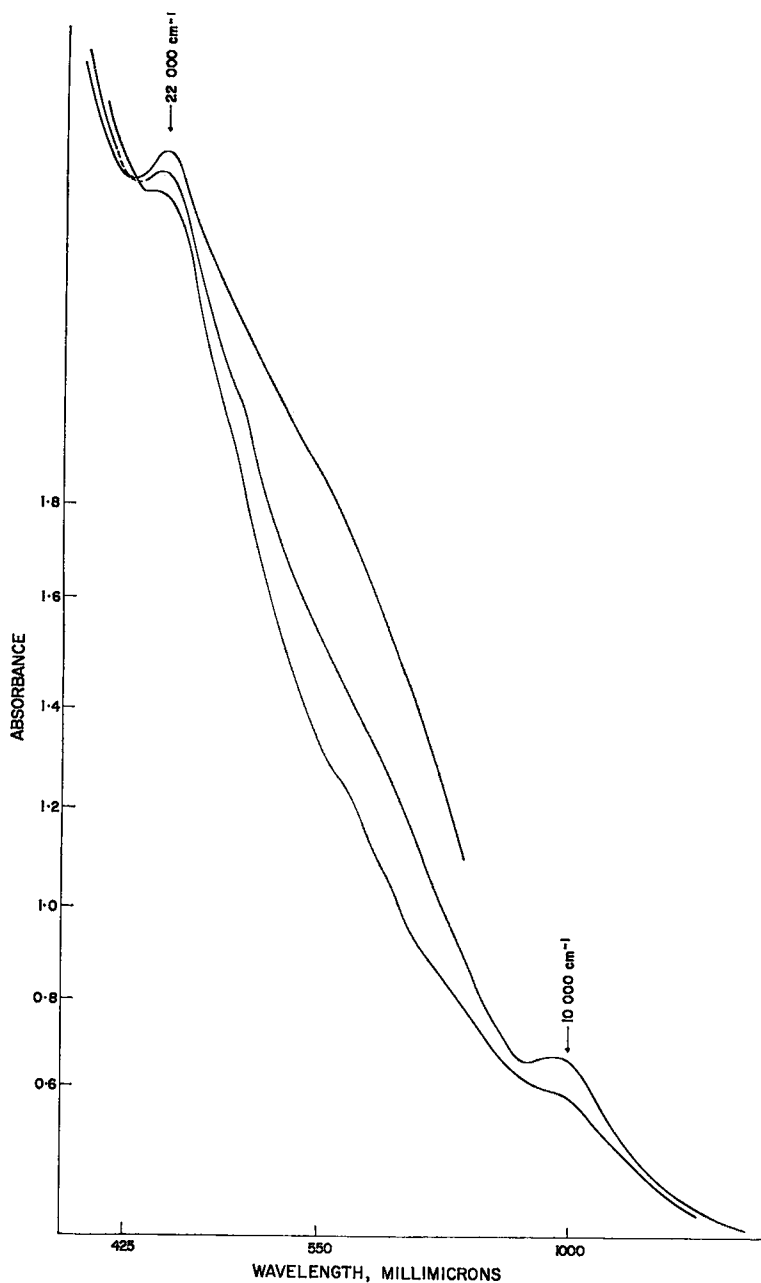


FIG. 4. Absorption spectrum of an  $a$ - $b$  (001) section of titanaugite. Upper curve is  $E \parallel b$  spectrum showing prominent broad band at  $\sim 600 \text{ m}\mu$ , lower curve is  $E \parallel a$  spectrum, and centre curve is unpolarised-light spectrum, in a section 0.0125 cm thick.

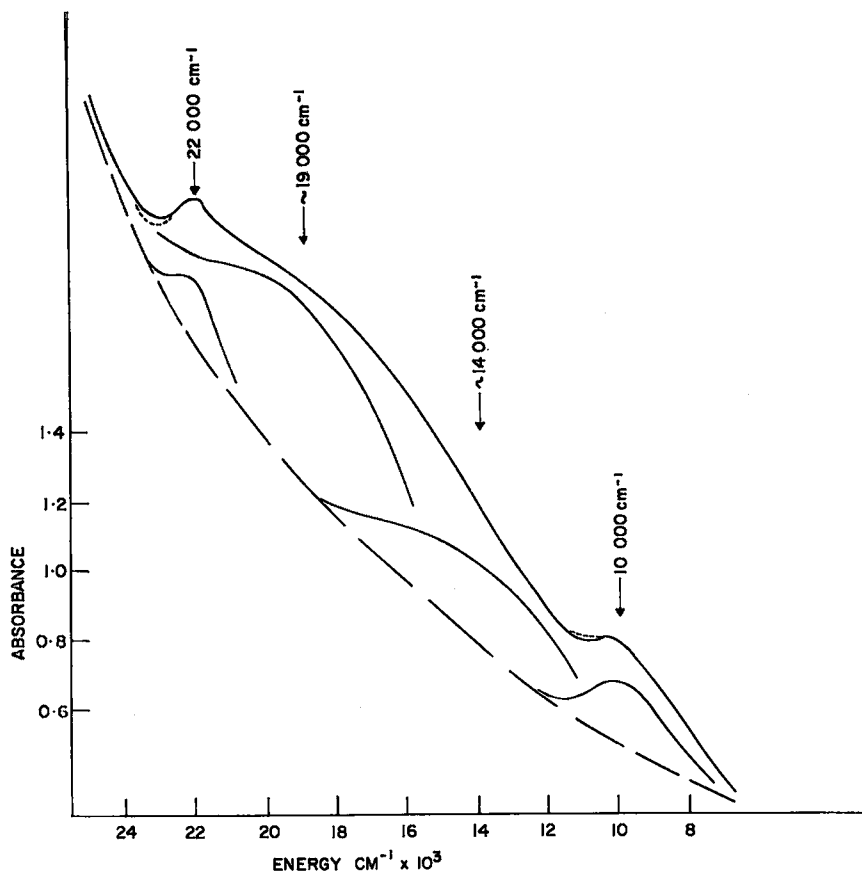


FIG. 5. Absorption spectrum of cleavage section of titanaugite (top), 0.02 cm thick; the dashed curve represents the assumed absorption edge, and the intermediate curves represent the resolved peaks obtained with the Dupont curve analyzer.

A chemical analysis of a titanaugite from Sasbach in the Kaiserstuhl is reported in Dana (1911). The principal transition-metal ions present are Fe<sup>2+</sup> (3%), Fe<sup>3+</sup> (3.5%) and Ti (2.5%). Chemical analyses of titanaugites listed in Deer, Howie and Zussman (1962) show that high concentrations of Fe<sup>2+</sup>, Fe<sup>3+</sup> and Ti are invariably present. Our sample of titanaugite, the identity of which was confirmed by  $\alpha$ -ray diffraction, contained 6% total Fe and 2.8% Ti, in agreement with the published analysis.

With these cations in mind, and based on the conclusions of earlier papers (Robbins and Strens, 1968; Faye, Manning and Nickel, 1968;

Manning, 1968 *a, b*), the following electronic transitions could conceivably be observed in the titanaugite:

- (i)  ${}^5T_2 \rightarrow {}^5E(D)$  in octahedrally-bonded  $Fe^{2+}$ ; absorption bands expected in the near infrared region at  $\sim 10000\text{ cm}^{-1}$ , with  $\epsilon \sim 5\text{--}10$ .
- (ii)  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer; pleochroic absorption band expected in  $13500\text{--}17000\text{-cm}^{-1}$  range, with maximum intensity in  $E\parallel b$  spectra.
- (iii)  ${}^2T_2 \rightarrow {}^2E(D)$  in  $Ti^{3+}$ ; absorption band expected in  $17000\text{--}20000\text{ cm}^{-1}$  range (see also Manning, 1967 *a*).
- (iv)  ${}^6A_1 \rightarrow {}^4A_1E(G)$  transition in  $Fe^{3+}$ ; probably in the range  $21800\text{--}23000\text{ cm}^{-1}$  (see also Manning, 1967 *a, b*); band expected to be sharper than others in spectrum because this transition is field-independent.
- (v)  $Ti^{3+} \rightarrow Ti^{4+}$  charge-transfer; pleochroic band expected at  $22000\text{--}23000\text{ cm}^{-1}$ , with maximum intensity in  $E\parallel b$  spectra and minimum in  $E\parallel a$ .

Therefore, there seems ample justification in assigning the  $10000\text{ cm}^{-1}$  band with  $\epsilon \sim 10$  to  $Fe^{2+}$  (*i*), the  $\sim 14000\text{ cm}^{-1}$  band to  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer (*ii*), the  $19000\text{ cm}^{-1}$  band to  $Ti^{3+}$  (*iii*), and the  $22000\text{-cm}^{-1}$  band to  $Fe^{3+}$  (*iv*). Because the parent cations in augite and diopside are, for the most part, divalent, most of the Ti will likely be  $Ti^{3+}$ , and the low  $Ti^{4+}$  content is probably reflected in the absence of a pleochroic band at  $22000\text{ cm}^{-1}$  in titanaugite. The  $\epsilon$ -value of the  $22000\text{ cm}^{-1}$  band, based on an  $Fe^{3+}$  concentration of  $\sim 3.5\%$  is in the range  $5\text{--}10$  litres/mole $\cdot$ cm, indicating that, as in riebeckite, the band gains intensity from its proximity to intense charge-transfer bands.

The pleochroism of titanaugite would seem to be due mainly to  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer, while the colour is due to transitions (*ii*)–(*iv*), above, superimposed on the limb of the ultra-violet absorption edge.

### CONCLUSIONS

Absorption bands in the spectrum of a titanaugite from Kaiserstuhl, Germany, have been assigned to  $d\text{--}d$  electronic transitions in  $Fe^{2+}$ ,  $Fe^{3+}$  and  $Ti^{3+}$ , and also to  $Fe^{2+} \rightarrow Fe^{3+}$  charge-transfer. The pleochroism of titanaugite is due in the main to the last-mentioned process. All these electronic transitions, except those in  $Fe^{2+}$ , are observed in the visible region, and together with the limb of absorption edge, account for the colour of titanaugite.

A pleochroic absorption band, polarized along  $Fe^{2+} \rightarrow Fe^{3+}$  directions, is the obvious main contributor to the colour and pleochroism of a riebeckite from St. Peter's Dome, El Paso County, Colorado. The band

marks  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge-transfer, and is observed at  $15700 \text{ cm}^{-1}$ . A relatively weak, sharp peak at  $23000 \text{ cm}^{-1}$  is assigned to the  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1$   $\text{E}(\text{G})$  transition in  $\text{Fe}^{3+}$ . The latter band borrows intensity from the intense  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge-transfer band.

The presence of the  $\text{Fe}^{3+}$   $d-d$  band at  $23000 \text{ cm}^{-1}$  in riebeckite spectra shows that the  $d$ -electron is localized on the  $\text{Fe}^{2+}$  ion, *i.e.*,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  exist as discrete ions in riebeckite. In the riebeckite specimen, each  $\text{Fe}^{3+}$  ion has on average a  $\text{Fe}^{2+}$  neighbour.

#### ACKNOWLEDGEMENTS

The authors wish to thank R. Craig of the Inorganic Chemistry Sub-division for performing the chemical analyses, H. R. Steacy, curator of the National Mineral Collection, for the loan of the sample of riebeckite, and H. V. Morley of the Department of Agriculture for the use of the Dupont curve analyser. Discussions with G. H. Faye are also gratefully acknowledged.

#### REFERENCES

- BRAGG, W. L. (1937): *The Atomic Structure of Minerals*. Cornell Univ. Press.
- BURNS, R. G. (1965): *Electronic Spectra of Silicate Minerals*. Ph.D. Diss., Univ. California, Berkeley, California.
- BURNS, R. G. & FYFE, W. S. (1967): Crystal-field theory and the geochemistry of transition elements. *Researches in Geochemistry* **2**, 259-285. John Wiley and Sons, New York.
- BURNS, R. G. and PRENTICE, F. J. (1968): Distribution of iron cations in the crocidolite structure. *Amer. Mineral.* **53**, 770-776.
- BURNS, R. G. & STRENS, R. G. J. (1967): Structural interpretation of polarised absorption spectra of the Al-Fe-Mn-Cr epidotes. *Min. Mag.* **36**, 204-226.
- COTTON, F. A. & WILKINSON, G. (1967): *Advanced Inorganic Chemistry*. Interscience Publishers, New York.
- DANA, E. S. (1911): *Descriptive Mineralogy*. 6th Ed., p. 361.
- DAY, M. C. & SELBIN, J. (1962): *Theoretical Inorganic Chemistry*. Reinhold Publishing Corp., New York.
- DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals*, vol. **2**. Longmans, Green and Co. Ltd., London.
- ENGLMAN, R. (1960). Charge transfer states and optical absorption in octahedrally hydrated paramagnetic salts. *Mol. Phys.* **3**, 48-58.
- FAYE, G. H. (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. (1968b): 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.
- FAYE, G. H., MANNING, P. G. & NICKEL, E. H. (1968): An interpretation of the polarised optical absorption spectra of tourmaline, cordierite, chloritoid and vivianite:  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  electronic interaction as a source of pleochroism. *Am. Mineral.* **53**, 1174-1201.
- FIGGIS, B. N. (1966): *Introduction to Ligand Fields*. Interscience Publishers, New York.
- HARTMANN, H. & SCHLAFFER, H. L. (1951): Colour and constitution of complex compounds. II. Light absorption of complex ions of Ti(III). *Z. phys. Chem. (Leipzig)* **197**, 116-142.

- KUNITZ, W. (1930): Die isomorphieverhältnisse in der Hornblendegruppe. *Neues Jahrb. Min.* **A60**, 171-250.
- LITTLER, J. G. F. & WILLIAMS, R. J. P. (1965): Electrical and optical properties of crocidolite and some other iron compounds. *J. Chem. Soc.* **1965**, 6368-6371.
- MANNING, P. G. (1967a): The optical absorption spectra of some andradites and the identification of the  ${}^6A_1 \rightarrow {}^4A_1E(G)$  transition in octahedrally-bonded  $Fe^{3+}$ . *Can. J. Earth Sci.* **4**, 1039-1047.
- MANNING, P. G. (1967b): The optical absorption spectra of the garnets almandine-pyrope, pyrope and spessartine and some structural interpretations of mineralogical significance. *Can. Mineral.* **9**, 237-251.
- MANNING, P. G. (1968a): On the origin of colour and pleochroism of astrophyllite and brown clintonite. *Can. Mineral.* **9**, 663-677.
- MANNING, P. G. (1968b): An optical absorption study of the origin of colour and pleochroism in pink and brown tourmalines. *Can. Mineral.* **9**, 678-698.
- ROBBINS, D. W. & STRENS, R. G. J. (1968): Polarization-dependence and oscillator strengths of metal-metal charge-transfer bands in iron(II, III) silicate minerals. *Chem. Comm.* **1968**, 508-509.
- TANABE, Y. & SUGANO, S. (1954): On the absorption spectra of complex ions. *J. Phys. Soc. Japan*, **9**, 753-766.
- WARREN, B. E. & BRAGG, W. L. (1928): The structure of diopside,  $CaMg(SiO_3)_2$ . *Zeit. Krist.* **69**, 168-193.
- WHITTAKER, E. J. W. (1949): The structure of Bolivian crocidolite. *Acta. Cryst.* **2**, 312-317.

*Manuscript received September 23, 1968, emended January 23, 1969*

### M.A.C. BRIEF TO THE SCIENCE SECRETARIAT

The executive committee of the Mineralogical Association of Canada has submitted a brief to the study group commissioned by the science secretariat to assist the Science Council of Canada in developing recommendations for future research in the earth sciences. Copies of the brief, which runs to eleven pages, can be obtained from Mr. J. F. Rowland, Secretary, Mineralogical Association of Canada, Mines Branch, 555 Booth Street, Ottawa 4, Ont.