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THE OPTICAL ABSORPTION SPECTRA OF TOURMALINE: IMPORTANCE OF CHARGE-TRANSFER PROCESSES

G. H. FAYE*, P. G. MANNING**, J. R. GOSSELIN* AND R. J. TREMBLAY***

ABSTRACT

Optical absorption spectra resolved into Gaussian bands, Mössbauer spectra, and electron-microprobe analyses are collated for several tourmalines in the elbaite–schorl and dravite–schorl series. This work clarifies the scattered and previously puzzling information on spectral features that affect the colours and pleochroism of tourmaline.

Emphasis is placed on the identification and importance of the $O^{2-} \rightarrow Fe^{2+}$ (Fe^{3+}), $Fe^{2+} \rightarrow Fe^{3+}$, and $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer processes. These processes are mainly responsible for the dichroism of tourmaline. The metal–metal interactions are facilitated when the electric vector of incident light vibrates in the 0001 plane. Ultraviolet-centered $O^{2-} \rightarrow Fe^{2+}$ and $O^{2-} \rightarrow Fe^{3+}$ processes are intensified by the replacement of OH^- by O^{2-}, for example when Ti^{4+} substitutes into octahedral sites of tourmaline. The former process is important in the colouring of Ti-rich dravites whereas the latter strongly influences the spectrum of schorls. The resolved, visible-region spectra of blue and black tourmalines are qualitatively remarkably similar and both have a prominent absorption at ~18,500 cm^{-1} which, through a heating experiment and Mössbauer measurements, has been identified as the $Fe^{2+} \rightarrow Fe^{3+}$ process. The brown colour of Ti-rich dravites is also influenced by strong $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer absorption at 22,000 - 24,000 cm^{-1}, and a weaker version of the band contributes to the green colour of elbaites.

The polarization properties of the Fe^{2+} *d-d* bands, which have maximum intensity in $E \perp c$ spectra of coloured varieties, arise from intensity borrowing from $O^{2-} \rightarrow Fe^{2+}$ charge-transfer. Near-infrared spectra of specimens in the elbaite-schorl series show, on curve-resolution, previously undiscovered bands that mark the presence of Fe^{2+} in the *c*-site. These "new" features are strong in the spectra of black (schorl) specimens but weak for specimens near the elbaite end of the elbaite-schorl join.

INTRODUCTION

Although the chemistry and structure of tourmaline are well-known, the optical absorption spectra continue to defy a satisfactory unified interpretation. It is generally accepted that the two prominent absorptions at ~9,000 and ~14,000 cm^{-1} in tourmaline spectra are components of the $^5T_2 \rightarrow {}^5E(D)$ transition in Fe^{2+} ions located principally in the brucite-type *b*-sites (Faye *et al.* 1968; Townsend 1970; Wilkins *et al.* 1969; Manning 1969a). However, it has been argued that the two bands arise from Fe^{2+} ions located in the *b*- and Al *c*-sites, respectively (Burns 1972; Burns & Simon 1973), but this seems improbable because the relative intensities of the two bands are remarkably constant for differently-coloured varieties.

The origin of the numerous dichroic absorption bands in the visible region spectra (~700 nm to ~400 nm) of tourmalines is poorly understood. Strongly-polarized broad bands at ~22,000 cm^{-1} (450 nm) in spectra of green and brown varieties have been assigned to $Ti^{3+} \rightarrow Ti^{4+}$ intervalence charge-transfer in the 0001 plane (Manning 1969b; Faye *et al.* 1968). Townsend (1970) feels the dichroism of tourmalines arises partly from charge-transfer transitions between metal ions sharing octahedral edges, and cited the suggestion that a dichroic shoulder at ~ 17,500 cm^{-1} in spectra of some blue-green varieties may well represent $Fe^{2+} \rightarrow Fe^{3+}$ interaction. On the other hand, Wilkins *et al.* (1969) attribute the colours of tourmalines to crystal-field transitions within Fe^{2+}, Fe^{3+} and Mn ions, but they ignored absorptions due to Ti and intervalence charge-transfer. Some of their assignments are suspect; for example, the prominent polarized band at 22,000 cm^{-1} in spectra of brown tourmalines is assigned to the field-independent transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in Fe^{3+}, and yet the band half-width of 5,500 cm^{-1} is unacceptably large (Manning 1969b). Crystal-field transitions within Cr^{3+} and Mn^{3+} are responsible for the colours of some deep-green and pink tourmalines (Manning 1969a,b); these varieties are not considered here because their spectra are understood reasonably well.

The complex structure of tourmaline inevitably introduces a considerable speculative element into spectral interpretation. Crystal-field bands of Fe, Mn and Ti ions often present in two valence states and distributed over two different octahedral sites and possibly a tetrahedral site, are superimposed on strong interval-

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*Research Scientists, and *** Technician, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, 555 Booth Street, Ottawa, Canada; and **Research Scientist, Inland Waters Branch, Department of the Environment, 562 Booth Street, Ottawa, Canada, K1A 0G1.

TABLE 1. ELECTRON MICROPROBE ANALYSES AND CELL PARAMETERS OF TOURMALINES*

Specimen	Locality	Colour	weight %			cell parameters	
			Fe	Ti	Mn	a (Å)	c (Å)
schorl	Villeneuve, Quebec	black	12.0	0.2	0.6	16.010 (7)*	7.172 (4)
elbaite TB1-1	Minas Gerais, Brazil	blue	6.4	<0.01	0.3	15.908 (6)	7.127 (5)
elbaite TGr-2	unknown	green	5.0	0.01	0.8	15.886 (6)	7.120 (4)
brown dravite no. 1	Gouverneur, New York	brown	1.1	0.7	0.05	15.966 (5)	7.204 (3)
brown tourmaline no. 2	unknown	yellow-brown	4.9	1.0	--	--	--
elbaite TZ - zone A	unknown	brownish-green	2.7	0.09	2.2	15.862 (5)	7.121 (3)
elbaite TZ - zone B	unknown	blue	2.8	0.02	2.0	15.857 (7)	7.129 (7)
elbaite TZ - zone D	unknown	brown	3.3	0.10	1.9	15.890 (7)	7.134 (5)
elbaite TZ - zone F	unknown	light green	2.0	0.04	1.7	15.832 (7)	7.129 (4)

*Figure in parenthesis gives the standard deviation of the last digit.

TABLE 2. MÖSSBAUER DATA FOR CERTAIN TOURMALINES

	isomer shift, mm/s (rel. to Fe powder)	quadrupole splitting, 2ε mm/s	line width at half-height, mm/s	relative intensities, %	oxidation state of Fe	Fe^{2+}/Fe^{3+}	site distr. of Fe^{2+} b:a
schorl	1.1	2.2	0.4	40	2+	3:1	8:7
	0.7	1.5	0.6	35	2+		
	0.3	0.8	0.5	25	3+		
elbaite TB1-1	1.0	2.4	0.4	90	2+	~24:1	~15:1
	1.0	1.4	0.4	6	2+		
	-	-	-	~4	3+		
elbaite TB1-1, heated	1.1	2.4	0.5	53	2+	2:1	9:2
	1.0	1.7	0.5	12	2+		
	0.3	0.9	0.5	23	3+		
	0.4	1.1	0.5	12	3+		
elbaite TGr-2	1.1	2.3	0.4	80	2+		
	1.3	2.2	0.4	20	2+		
	-	-	-	<2			

ence charge-transfer bands arising from different combinations of adjacent donor-acceptor metal ions (Fe^{2+} and Fe^{3+}, Fe^{2+} and Ti^{4+}, Ti^{3+} and Ti^{4+}) located in b-b sites (absorption polarized $E \perp c$), b-c sites (polarized $E \perp c$) and c-c sites (maximum intensity $E \| c$), as well as on oxygen → metal charge-transfer bands originating in the uv region. Insufficient attention has been paid to accurate curve-resolution of spectra in the optical region. Further, chemical analyses by electronmicroprobe do not yield metal valence states directly.

In the current work, the optical spectra of a suite of brown, green, blue, and black tourmalines and of a crystal zoned in most of the above colours, have been collated, resolved into component absorptions, and related to Fe and Ti content Mössbauer obsorption and heating experiments are also described. A basis is presented for a unified theory of interpretation of spectra of tourmalines of the dravite-schorl series; charge-transfer processes are shown to be predominant.

Experimental Details

Specimens

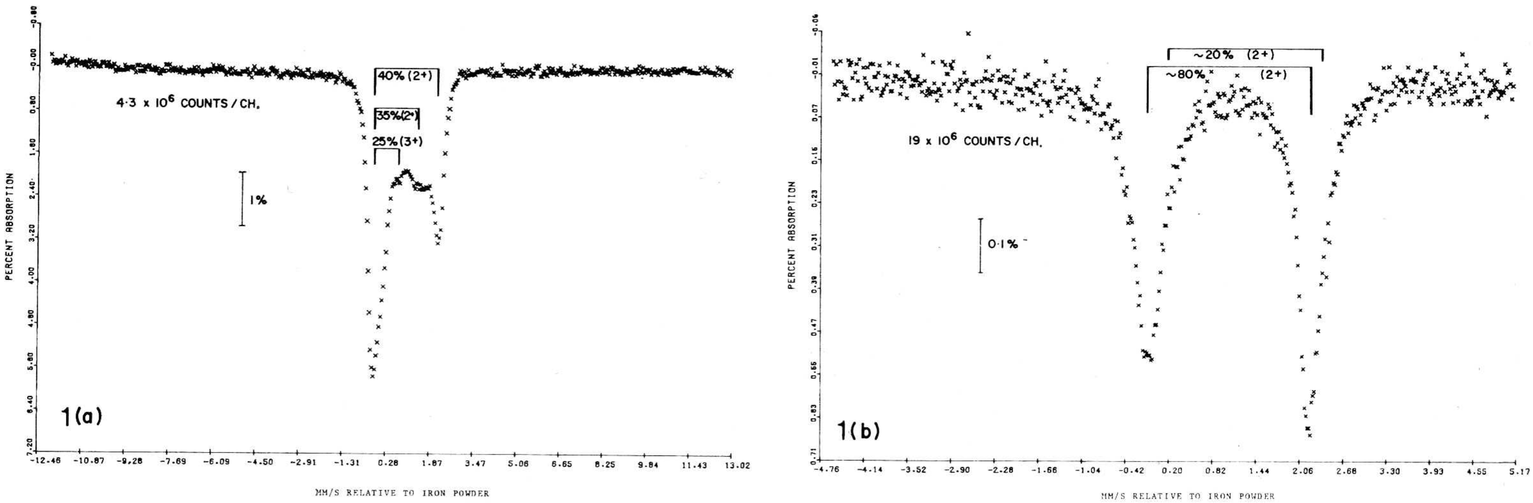
The tourmaline specimens were obtained through the courtesy of Mr. H. R. Steacy, curator of the reference series of the National Mineral Collection, Geological Survey of Canada. The results of partial analysis by electron microprobe (D. R. Owens), and the cell dimensions of powdered samples, as measured by x-ray diffraction using a 114.6 mm Debye-Scherrer camera (J. M. Stewart) are given in Table 1.

The varietal names were selected according to the cell parameters and the nearest end-member in the elbaite-schorl or dravite-schorl series.

Mössbauer spectra

The Mössbauer spectra are shown in Figures 1 and 2; they were obtained at room temperature with a spectrometer having a velocity drive of the constant acceleration type, synchronized by a 512-channel analyzer. The source was ^{57}Co diffused in copper. The velocity scale was calibrated, using iron powder as a standard, immediately ofter the measurement of the spectrum of each sample. The linewidth from the calibration spectrum varied from 0.3 to 0.4 mm/sec, averaging 0.37 mm/sec.

The spectra were computer-fitted (D. W. Carson) to a selected number of Lorentzian line profiles by a least-squares method and correction was made for the parabolic background (intensity variations at the detector due to source motion). The typical linewidth resulting from these fits was appreciably larger than the calibration linewidth. This implies a spread in the Mössbauer parameters of the underlying spectra and this bears directly on the interpretations given here. Because the measurements were



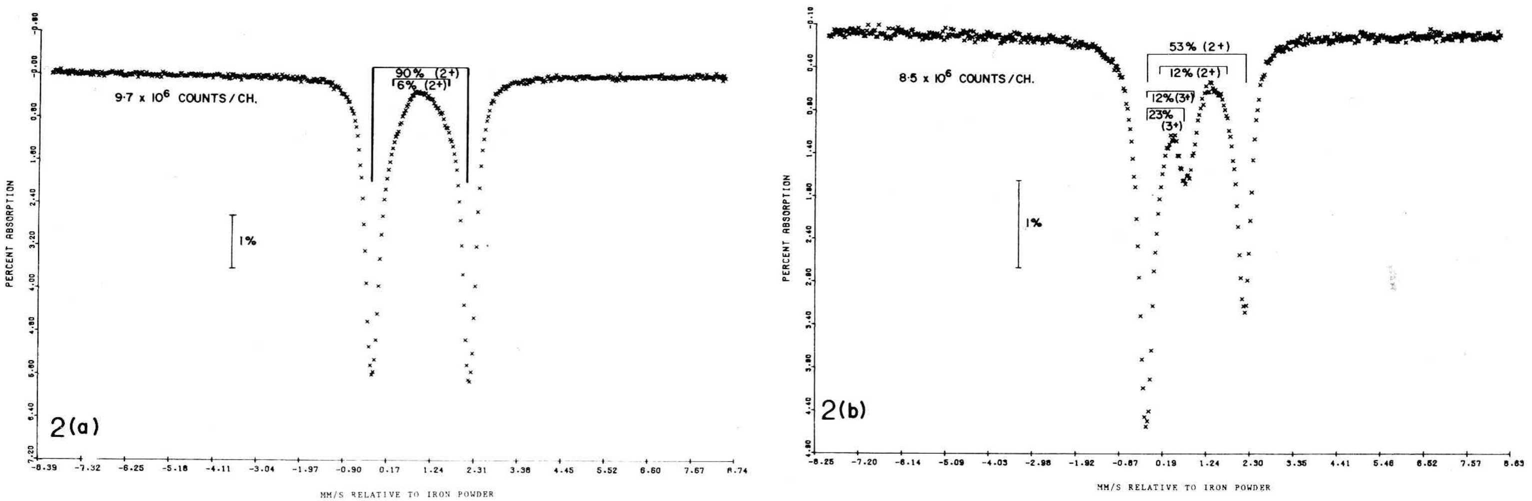


FIG. 1. Mössbauer spectra of: (a) schorl, (b) elbaite TGr-2.

FIG. 2. Mössbauter spectra of: (a) elbaite TB1-1 before heating, (b) TB1-1 after heating in air for 20 hr at 800°C.

not of an absolute nature, the Mössbauer fraction for each tourmaline site is unknown; however, for this work, it was assumed to be uniform. This is necessary to relate directly a given peak area to the population of iron ions responsible for that absorption peak. The components of the spectra are doublets and they are assumed to be symmetrical in peak-area.

The smoothness of the low-velocity peak of the schorl spectrum of Figure 1a precludes the objective separation of the component-peaks; we have therefore ascribed the centroid velocity to each component-peak, thereby introducing an additional uncertainty ($<\pm 0.1$ mm/sec) in the isomer shift of these doublets.

Although the value of 0.7 mm/sec (Table 2) for the isomer shift for the second schorl doublet is at the lower end of the range for Fe^{2+}, the corresponding quadrupole splitting is definitely too high for Fe^{3+} (Goldanskii 1964). We therefore ascribe this doublet to Fe^{2+}.

As a basis for peak assignments it was assumed that, with respect to the iron powder standard, Fe^{3+} would not exhibit a peak above 1 mm/sec (Goldanskii 1964).

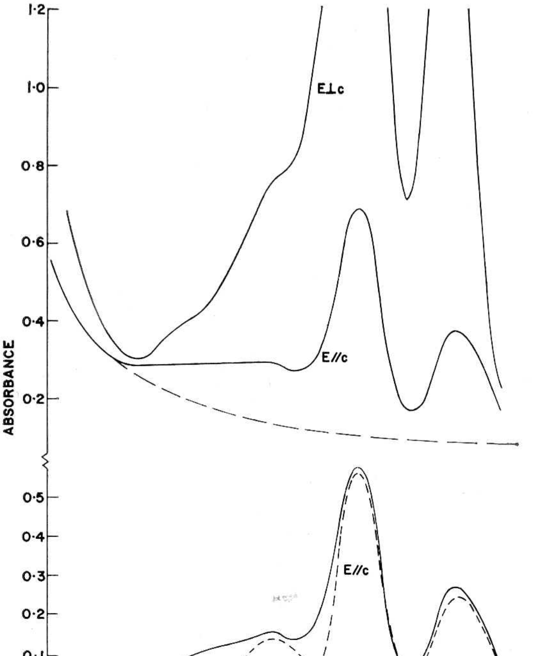


FIG. 3. Polarized spectra of blue tourmaline TB1-1, specimen thickness 0.046 cm. The $E||c$ spectrum was resolved after subtraction of the visually-judged background absorption (indicated by dashes).

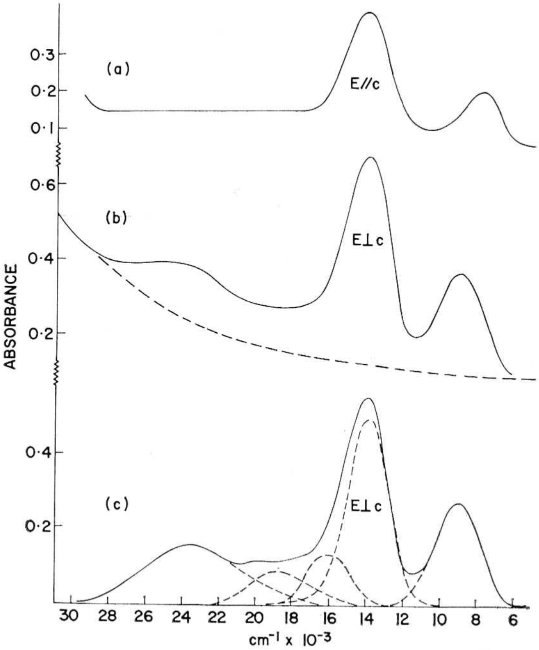


FIG. 4. Polarized spectra of elbaite TGr-2, specimen thickness 0.028 cm. (a) $E||c$ spectrum, (b) unresolved $E\perp c$ spectrum with visually-judged background absorption indicated by dashes, (c) resolved $E\perp c$ spectrum after subtraction of background.

Absorption spectra

Absorption spectra of rational sections of tourmaline were measured at room temperature with a Cary 14H spectrophotometer. Polarized spectra were obtained by placing matched Nicol prisms in the sample- and reference beams, each prism being mounted in the well of a specimen holder.

Extraction coefficients (ϵ) for absorption bands were calculated from

$$\epsilon = A/C.\ l \text{ (in litres/mole-cm)}$$

where A = net absorbance, C = cation concentration in moles/litre (Tables 1 and 2), and l = sample thickness in cm.

Absorption coefficients (Fig. 10) were calculated from

$$\alpha = \frac{A}{l} \text{ (in cm}^{-1}\text{)}$$

where A and l have the same significance as above.

Resolved spectra (Figs. 3, 4c, 5b, and 6) were obtained by re-plotting the original spectrograms on a linear energy scale, subtracting a

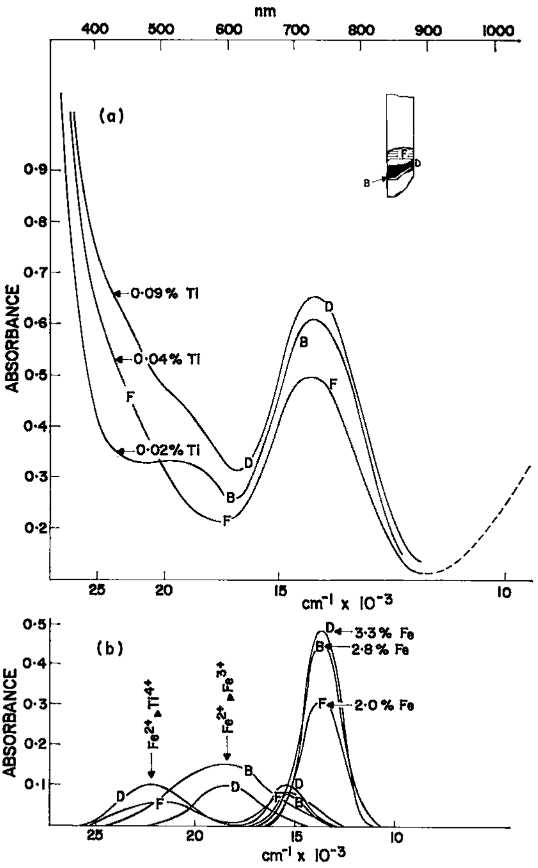


FIG. 5. Unpolarized spectra of zoned tourmaline TZ, specimen thickness 0.066 cm. (a) original unresolved spectra, non-linear energy scale, (b) resolved spectra, linear energy scale. Zone D 2.7% Fe, 0.09% Ti; Zone F 2.0% Fe, 0.04% Ti; Zone B 2.8% Fe, 0.02% Ti.

visually-judged background absorption, and then resolving the net spectra with a Dupont Model 310 curve resolver. Although this technique is somewhat subjective, it is considered that the position of the minor "hidden" features are probably accurate to within ± 300 cm^{-1}. Intensity values are subject to errors of approximately ± 25%.

DESCRIPTION AND DISCUSSION OF OPTICAL SPECTRA

The crystal-field bands of Fe^{2+} in tourmaline — evidence for Fe^{2+} in the c-site

Mössbauer measurements in this and other studies (Marfunin 1970; Burns 1972; Burns & Simon 1973; Hermon *et al.* 1973) demonstrate that Fe^{2+} is present in both *b*- and *c*-sites of tourmalines in the dravite–schorl and elbaite–schorl series. The *b*:*c* occupancy ratio of Fe^{2+} varies from ~1:1 for the black Villeneuve specimen to ~15:1 for some elbaites (Table 2, Hermon *et al.* 1973).

Despite Mössbauer evidence for Fe^{2+} occupancy of the two sites, absorption spectra seem to show only the two commonly-observed near-infared bands arising from components of the $^5T_2 \rightarrow {}^5E$ transition of Fe^{2+} in one distorted octahedral site. Because the average dimensions of the *c*-sites (Al-O = 1.93Å) in dravites, for example, are substantially smaller than those of the *b*-sites (Mg-O = 2.05Å) (Buerger *et al.* 1962), it is anticipated that additional bands that can be assigned to Fe^{2+} ions in the smaller *c*-sites should be seen at higher energy. Indeed Marfunin (1970) has suggested, from unresolved spectra of several black tourmalines, that a band at ~12,000 cm^{-1} is due to Fe^{2+} in the *c*-site having C_{3v} symmetry. As will be seen, such a band was not found in resolved spectra of the present work.

Resolution of the two envelopes centred at ~13,800 cm^{-1} (725 nm) and ~8,600 cm^{-1} (1160 nm) in spectra of the Villeneuve tourmaline (Fig. 6) reveals that each comprises two bands, at ~13,200 cm^{-1} and ~14,500 cm^{-1} in the former envelope, and at ~7,900 cm^{-1} and ~9,500 cm^{-1} in the latter. Pairing the components at 14,500 cm^{-1} and 9,500 cm^{-1} and those at 13,200 cm^{-1} and 7,900 cm^{-1}, and averaging the energies of the two components of each pair, it can be argued (Faye 1972) that the corresponding Fe^{2+}-O distances in the *c*- and *b*-sites are respectively 2.03 to 2.05Å and 2.09 to 2.11Å. The two pairs are of approximately equal intensity, consistent with Mössbauer-derived (Table 2) Fe^{2+} *b*:*c* populations of ~1:1.

Burns & Simon (1973) have suggested that the bands near 14,000 cm^{-1} and 9,000 cm^{-1} are due to Fe^{2+} in the *c*- and *b*-sites respectively. However, this seems to be disproved by the present work in that the schorl spectrum in Figure 6 shows four crystal-field bands that must belong to Fe^{2+} in *b*- and *c*-sites, and Mössbauer spectra of TB1-1 shows a 15:1 ratio of Fe^{2+} in *b*:*c* and yet the 14,000:9,000 cm^{-1} absorbance ratio is not greatly different from that of schorl for which *b*:*c* = 8:7.

The band at ~6,000 cm^{-1} in Figure 6b is difficult to explain in terms of six-coordinate Fe^{2+}. However, it could be due to a small amount of Fe^{2+} in tetrahedral or eight-fold cubic coordina-

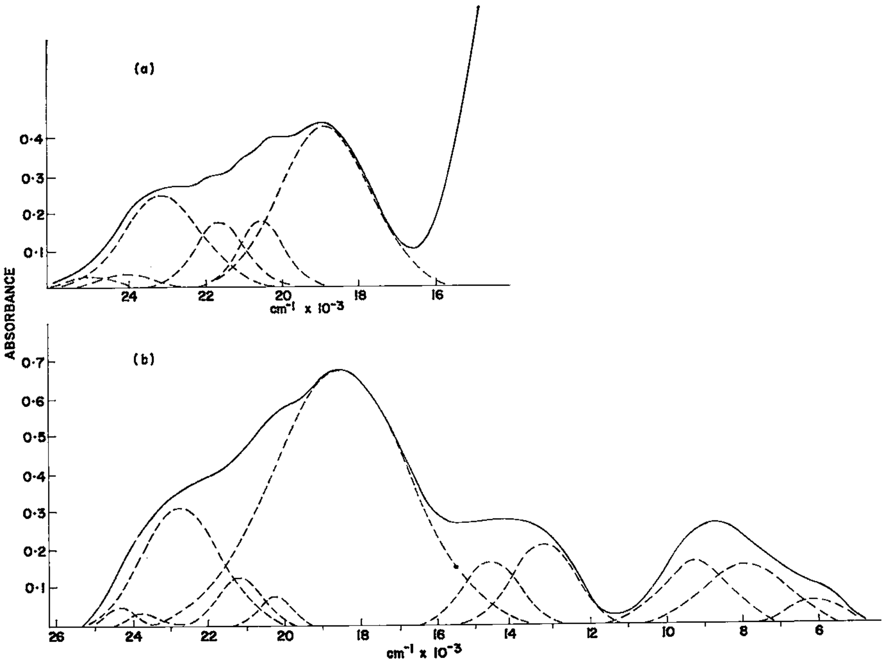


FIG. 6. Resolved unpolarized spectra of: (a) blue tourmaline TB1-1, specimen thickness 0.18 cm. (b) schorl, specimen thickness 0.011 cm.

tion; such species are known to absorb in the 6,000 cm^{-1} region (Burns 1970, pp. 60 and 85 respectively; White & Moore 1972).

Careful resolution of unpolarized and $E||c$ spectra ($E \perp c$ spectra are usually too intense to be resolved) of a number of elbaites indicates the presence of a weak band at 15,000-16,000 cm^{-1} that manifests itself only as a modest distortion from the symmetrical of the higher-energy Fe^{2+} band centered at ~14,000 cm^{-1} (Figs. 3, 4, and 5). There is less conclusive evidence for the presence of a second "hidden" band in elbaite spectra at 9,500-10,500 cm^{-1} (Fig. 3). If these two "hidden" bands are paired, their average energies (12,000-13,000 cm^{-1}) are appropriate for Fe^{2+}-O c-site distances of 2.03 - 2.05Å (Faye 1972). Mössbauer measurements of elbaites reveal relatively small amounts of Fe^{2+} ions in c-sites (Table 2). The intensities and energies of the "hidden" bands are uncertain because of difficulties in estimating the uv-centred background absorption. The lower energies of Fe^{2+} spectral bands in schorl compared with those of Fe^{2+} in elbaites are consistent with earlier observations (Burns 1970) that increasing Fe^{2+} substitution into relatively tight octahedral sites (*e.g.*, Mg) in ferromagnesian silicates causes an approximately linear decrease in *Dq*.

Effect of $O^{2-} \rightarrow Fe^{2+}$ and $O^{2-} \rightarrow Fe^{3+}$ charge-transfer on dichroism

The dichroism of tourmalines has been explained (Townsend 1970) on grounds that metal → metal (ϵ>100-1000) and oxygen → metal (ϵ>>1000) charge-transfer processes are promoted when the electric vector vibrates in the 0001 plane, which plane contains overlapping t_{2g} lobes of adjacent edge-sharing octahedra. Crystal-field transitions (ϵ~1-10) borrow intensity from charge-transfer transitions (Manning 1973) and here we wish to emphasize the degree to which uv-centred $O^{2} \rightarrow Fe^{2+}$ and $O^{2-} \rightarrow Fe^{3+}$ charge-transfer processes influence the dichroism in the visible and near-infrared regions. In ferromagnesian silicates, glasses, and aqueous solutions, the $O^{2-} \rightarrow Fe^{2+}$ and $O^{2-} \rightarrow Fe^{3+}$ processes are centred at 50,000-55,000 cm^{-1} and 40,000-50,000 cm^{-1}, respectively. For a mineral section of given thickness, the intensity, peak-centre and breadth of the charge-transfer bands depend not only on cation concentrations but also on such factors as the composition of second-nearest neighbour sites (Manning 1973). Because $O^{-2} \rightarrow Fe^{2+}$ absorption occurs at a higher energy than $O^{2-} \rightarrow Fe^{3+}$, and because the molar extinction coefficient for the former process is less than that for the latter (Steele & Douglas 1965) it follows that, for

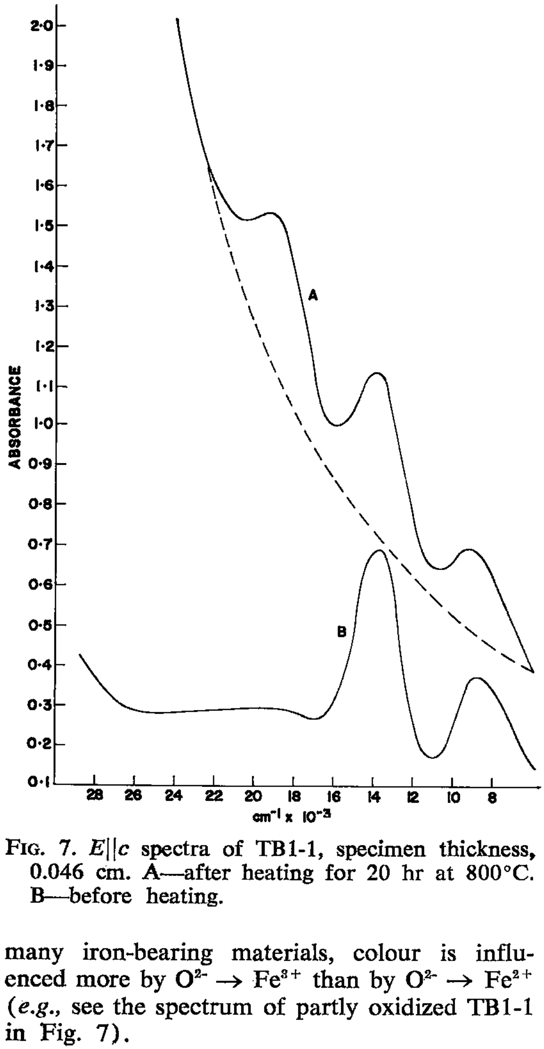


FIG. 7. $E||c$ spectra of TB1-1, specimen thickness, 0.046 cm. A—after heating for 20 hr at 800°C. B—before heating.

many iron-bearing materials, colour is influenced more by $O^{2-} \rightarrow Fe^{3+}$ than by $O^{2-} \rightarrow Fe^{2+}$ (*e.g.*, see the spectrum of partly oxidized TB1-1 in Fig. 7).

In Figure 8 is plotted the $E\perp c/E||c$ intensity ratio for the *b*-site Fe^{2+} band at 14,000 cm^{-1} against Fe^{2+} concentration for most of the specimens listed in Table 1 and also for a number of tourmalines described earlier (Wilkins *et al.* 1969). Ferrous ion populations for the Villeneuve schorl are known from Mössbauer spectra (Table 2), whereas, for the other tourmalines, it is assumed that the Fe^{2+} concentration is the total-Fe concentration. We propose that the approximately linear relationship in Figure 8 reflects the degree of intensity-stealing from $O^{2-} \rightarrow Fe^{2+}$ charge-transfer processes. In support of this, we have observed that the intensity ratio $E\perp c/E||c \simeq 1$ for the colourless tourmaline listed in Table 1, in which material, quite obviously, energy overlap between charge-transfer transitions and crystal-field transitions is negligible.

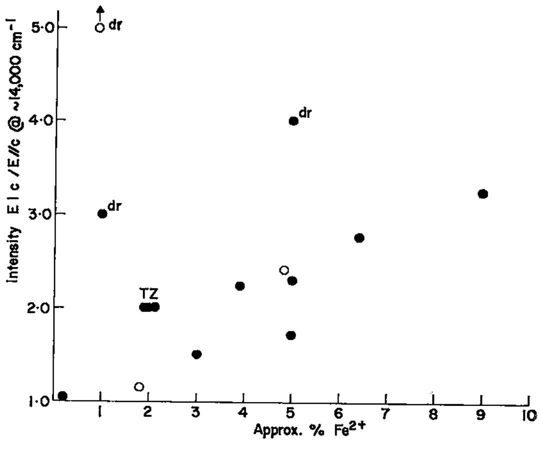


FIG. 8. Variation of intensity ratio $E\perp c/E||c$ of Fe^{2+} band at 14,000 cm^{-1} with Fe^{2+} concentration. o = calculated from spectra measured by Wilkins, Farrell & Naiman (1969). ● = calculated from spectra measured by the authors. dr = brown titaniferous dravites. TZ = zoned tourmaline containing titanium.

$Fe^{2+} \rightarrow Fe^{3+}$ *charge-transfer in tourmaline*

Questions as to whether the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process is of measurable intensity in tourmalines and as to which of a number of dichroic absorption bands characterizes the process have yet to be resolved (Faye *et al.* 1968; Wilkins *et al.* 1969; Townsend 1970; Burns 1972). However, remarkable similarities in the net visible-region absorption spectra (Fig. 6) of blue and black tourmalines (after subtracting uv-centred background and the high-energy limb of the 14,000 cm^{-1} band), and ad-

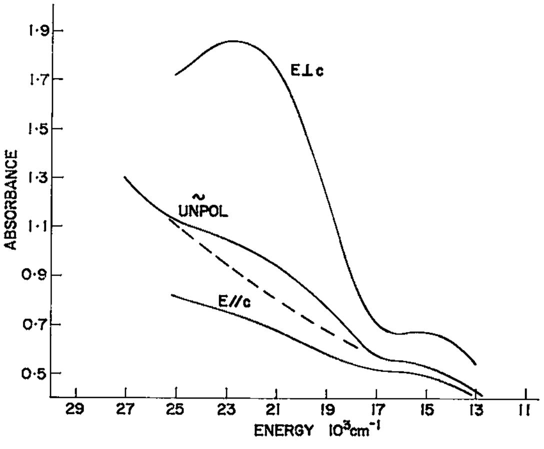


FIG. 9. Polarized spectra of brown dravite No. 1, specimen thickness 0.038 cm.

ditional similarities between the spectra of heated-blue (Fig. 7) and black (Manning 1969a, 1973) varieties, particularly in the 18,500 cm^{-1} region, indicate that the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band can be identified with confidence.

In most spectra presented in Figures 3, 4, and 5, absorptions at 17,500-19,000 cm^{-1} and 21,000-23,500 cm^{-1} can be recognized as metal-metal charge-transfer bands, firstly because they are clearly not part of the well-known crystal-field spectra of Fe^{3+}, Fe^{2+} or Mn^{2+} and, secondly, because the polarization properties (maximum intensity in $E \perp c$ spectra; see spectra of TB1-1 in Fig. 3 and of dravite in Fig. 9) are appropriate for M_b-M_b *and* M_b-M_c interaction. There is strong evidence that the 21,000-23,500 cm^{-1} band is associated with Ti (Manning 1969b; see also later text in current article). Therefore, the lower energy band is probably caused by $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer.

Spectra of blue (TB1-1) and black (Villeneuve) tourmalines

Figure 7 shows E||c spectra of TB1-1 before and after partial oxidation by heating in air at 800°C for 20 hours. The intensities of the absorption edge, probably caused by $O^{2-} \rightarrow Fe^{3+}$ charge-transfer, and of the 18,500 cm^{-1} band have increased dramatically on heating. Mössbauer measurements (Table 2) show that the Fe^{2+}/Fe^{3+} ratio changes from ~24:1 to ~2:1. Significantly, spectra of the Villeneuve tourmaline show a strong absorption at 18,500 cm^{-1} (Fig. 6) that is superimposed on intense uv-centred background (Manning 1969a, 1973), and here also, Mössbauer spectra indicate a low Fe^{2+}/Fe^{3+} ratio of ~3:1. It seems reasonable to conclude that the increased intensity of the 18,500 cm^{-1} band in spectra of heated-blue and of black tourmaline arises from an increased concentration of interacting Fe^{2+} - Fe^{3+} pairs, *i.e.*, the band represents $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer. It is to be noted that completely oxidized material at the surface of the heated TB1-1 specimen may also contribute to spectrum A of Figure 7; therefore, the spectral change on heating gives semi-quantitative information at best.

The Villeneuve tourmaline contains ~12% wt.% Fe, and the Fe^{2+}/Fe^{3+} ratio is ~3:1. Mössbauer spectra show that the Fe^{2+} is evenly distributed between the *b*- and *c*-sites (see Tables 1 and 2). Because of the low Ca content (0.11%) of the Villeneuve material, substitution of major amounts of Fe^{2+} into Al^{3+} *c*-sites requires parallel substitution of Fe^{3+} into M^{2+} *b*-sites; replacement of Na^{+} by Ca^{2+} is unimportant. Clearly, Fe^{3+} is localized for the most part on *b*-sites and $Fe^{2+} \rightarrow Fe^{3+}$ processes will occur in the 0001 plane ($E \perp c$). The polarization of the 18,500 cm^{-1} band for ($E \perp c$) is consistent with this expectation.

The five, possibly composite, bands in the 20,000-26,000 cm^{-1} range (Fig. 6) are difficult to assign, but the relatively small half-widths of most of them suggest that they mark spin-forbidden transitions in Fe^{2+} and Fe^{3+} ions which are only weakly field-dependent. The ϵ-values of the 22,500-23,500 cm^{-1} band, based on Fe^{3+} contents of TB1-1 and Villeneuve specimens, are 10 and 20, respectively. Corresponding values based on Fe^{2+} concentrations are 0.5 and 5. If this band is assigned to spin-forbidden transitions in Fe^{2+} or Fe^{3+}, the ϵ-values indicate intensity-borrowing from $O^{2-} \rightarrow Fe^{2+}/Fe^{3+}$ charge-transfer transitions, caused possibly by replacement of covalent next-nearest neighbour cations by less-covalent ions, *e.g.*, Si^{4+} by Al^{3+} or Fe^{3+} or, alternatively, by the conversion of OH^- to O^{2-} (Manning 1973). However, the uv-centred charge-transfer absorption in blue tourmaline spectra is not intense. Although the energy of the 22,500-23,500 cm^{-1} band is appropriate for the well-known transition ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in octahedral-Fe^{3+}, the band half-width (2,500-3,000 cm^{-1}) is too great for a field-independent transition, even allowing for the superimposition of two different Fe^{3+} spectra arising from two different next-nearest neighbour environments. The band could be similar to the 22,000-24,000 cm^{-1} band in spectra of green and brown tourmalines, the origin of which is discussed below.

It is noteworthy that Marfunin (1970) observed a band at ~18,000 cm^{-1}, in the spectra of several black tourmaline specimens, which he assigned to a spin-forbidden transition of Fe^{2+}.

$Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer in certain tourmalines

An absorption, in the form of a discrete band or a shoulder, is observed at 22,000-24,000 cm^{-1} in spectra of TGr-2 (Fig. 4), brown dravite (Fig. 9) and zones A, D and F of specimen TZ (Fig. 5). The band is particularly prominent in spectra of dravites that are Ti-rich but, compared to other tourmalines, relatively Fe-poor. The polarization properties of the band (maximum intensity when $E \perp c$) suggest metal-metal charge-transfer, possibly $Ti^{3+} \rightarrow Ti^{4+}$ as has been argued earlier (Manning 1969b) rather than the ${}^2T_2 \rightarrow {}^2E(D)$ transition in octahedral-Ti^{3+}. The Ti dependence of the band is illustrated beautifully by the analytical and spectral correlations of Figure 5.

The ϵ-values of the "Ti-band" in unpolarized-light spectra, based on total-Ti concentrations, range from ~15 for brown dravites, to ~100 for TGr-2, and to ~1000 in $E \perp c$ spectra of TGr-2 (Fig. 4). Because of the great dilution of 0.01% Ti (~0.01 molar) in TGr-2, corresponding to an occupancy of 0.002 sites out of 3.0 *b*-sites and 6.0 *c*-sites, the effective concentration of Ti^{3+} - Ti^{4+} pairs will be orders of magnitude less than 0.01 molar, from which the effective ϵ-value becomes unacceptably large ($> 10^4$) in $E \perp c$. Moreover, the absence of measurable Ti^{3+} *d-d* absorption in dravites, one of which contained 1% Ti and 1% Fe, the presence of strong Fe^{2+} *d-d* bands, and the expectation that ϵ-values of Ti^{3+} *d-d* bands are greater than those of Fe^{2+}, suggest that essentially all Ti in tourmalines is Ti^{4+}. These observations indicate that the 22,000-24,000 cm^{-1} band in brown and green tourmalines arises from $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer. The 22,500-23,500 cm^{-1} bands in TB1-1 and Villeneuve spectra are considerably narrower than the "Ti band" of dravites, 2,500 cm^{-1} against 5,500 cm^{-1} and this, combined with the low Ti concentration (<0.01%) of TB1-1, makes assignment difficult. It has been suggested that $Fe^{2+} \rightarrow Ti^{4+}$ processes cause absorptions in visible-region spectra of biotites and phlogopites (Faye 1968), synthetic and natural sapphires (Townsend 1968; Ferguson & Fielding 1971), natural pyroxenes (Dowty & Clark 1973) and synthetic glasses (van der Graf *et al.* 1973). Also, charge-transfer between Ti^{4+} and various inorganic ions, including Fe^{2+}, occurs in aqueous solutions (Reynolds 1965).

Effect of Ti^{4+} on the intensity of $O^{2-} \rightarrow Fe^{2+}$ charge-transfer

Robbins & Strens (1972) have shown that the substitution of Ti into the brucite layer of trioctahedral micas causes chemically and electronically distinct configurations around adjacent Fe^{2+} ions, and that this "Ti-effect" in turn causes a broadening and intensification of $O^{2-} \rightarrow Fe^{2+}$ bands so that they encroach on the visible region and markedly influence the colour and pleochroism. We have shown earlier in this work that the relatively large $E \perp c / E \| c$ intensity ratios for the Fe^{2+} 14,000 cm^{-1} *d-d* band in Ti-rich dravites (Fig. 8) arise through intensity-stealing from intensified $O^{2+} \rightarrow Fe^{2+}$ uv-centred absorption. The effect of Ti ions on the intensity of the $O^{2-} \rightarrow Fe^{2+}$ and $O^{2-} \rightarrow Fe^{3+}$ absorp-

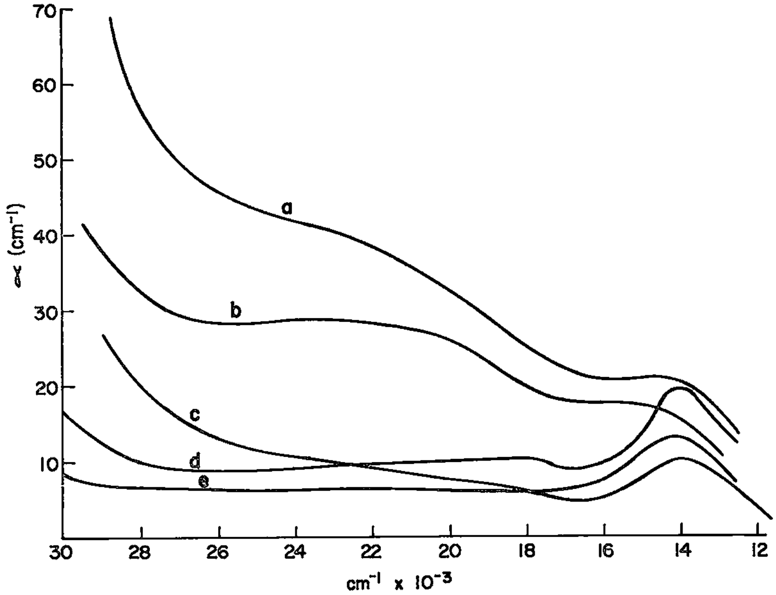


FIG. 10. Effect of titanium on intensity of uv charge-transfer (unpolarized spectra).

a = brown tourmaline — 4.9% Fe, 0.96% Ti.
b = dravite No. 1 — 1.0% Fe, 0.70% Ti.
c = TZ (zone D) — 3.3% Fe, 0.10% Ti.
d = TB1-1 — 6.0% Fe, <0.01% Ti.
e = TGr-2 — 5.0% Fe, 0.01% Ti.

tion is shown in Fig. 10 for different varieties of tourmalines. Because the Fe^{2+} concentration in these tourmalines greatly exceeds that of Fe^{3+}, we feel that $O^{2-} \rightarrow Fe^{2+}$ charge-transfer contributes the more to the absorption edge.

A "Ti-effect" has been observed from comparisons of spectra of green andradite and black schorlomite, garnets of respective composition $Ca_6(Fe^{3+}{}_{3.95}Mn_{0.05})Si_{6.0}O_{24}$ and $Ca_6(Fe^{3+}{}_{1.5}Al_{0.65}$-$Ti^{4+}{}_{1.83})$ $(Si_{4.5}Fe^{3+}{}_{0.95}Al_{0.39})O_{24}$, (Manning 1973). Oxygen→ Fe^{3+} charge-transfer and Fe^{3+} *d-d* bands are intensified in schorlomite by replacement of adjacent covalent Si^{4+} ions by less-covalent Fe^{3+} and Al^{3+} ions. Similarly, the substitution of Ti^{4+} into the *b*- or *c*-sites of tourmaline requires parallel charge-compensation, and this may be accomplished by conversion of $OH^- \rightarrow O^{2-}$. The O^{2-} ion is probably larger than OH^- and more polarizable, thus facilitating oxygen → metal charge-transfer. Cations in *b*-sites are normally bonded to two OH^- and those in *c*-sites to one OH^-. Significantly, O(3) site occupancies for some specimens of Donnay & Barton (1972) are $(OH)_{0.89}O_{0.11}$ in elbaites, $(OH)_{0.85}O_{0.15}$ in dravites and $(OH)_{0.16}O_{0.84}$ in very intensely absorbing buergerite.

CONCLUSIONS

Although previous workers have studied the optical absorption spectra of tourmalines in the elbaite-schorl and dravite-schorl series, the important influence of charge-transfer processes on colour and dichroism has not been recognized. This work has shown that these properties are due mainly to $O^{2-} \rightarrow Fe^{2+}$ (Fe^{3+}), $Fe^{2+} \rightarrow Fe^{3+}$ and $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer processes.

Blue and black tourmalines are strongly influenced by the $Fe^{2+} \rightarrow Fe^{3+}$ process at ~18,500 cm^{-1}, and the latter also by strong uv-centred $O^{2-} \rightarrow Fe^{3+}$ charge-transfer. The brown colour of Ti-rich dravites, and some elbaites, is due to a combination of uv-centred $O^{2-} \rightarrow Fe^{2+}$, and $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer at 22,000-24,000 cm^{-1}. The $Fe^{2+} \rightarrow Ti^{4+}$ absorption is relatively weak in green elbaites.

In general, the colour of a tourmaline, as determined by the intensity of the $Fe^{2+} \rightarrow Fe^{3+}$ band at ~18,500 cm^{-1}, is a good indicator of the degree of oxidation of iron according to the sequence: green-brown elbaites $\simeq$ brown dravites $<$ blue elbaites $<<$ black schorls.

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