OPTICAL ABSORPTION SPECTRA OF CHROMIUM-BEARING TOURMALINE, BLACK TOURMALINE AND BUERGERITE[1]

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ABSTRACT

Polarized absorption spectra are reported of Cr-bearing tourmaline from Kaavi, Finland, two black tourmalines from Villeneuve, Quebec and Como, Italy, and buergerite from San Luis Potosi, Mexico. Spectra of the Cr-bearing tourmaline exhibit two strong absorption bands at 17000 cm^{-1} and 24000 cm^{-1} that are characteristic of Cr^{3+}, the energy of the former band indicating that Cr^{3+} is located in a "loose site" in the octahedral sites in the spiral chain. For the most part, the spectra of the black tourmalines consist of bands marking transitions within Fe^{2+} and Fe^{3+} ions. A suggestion is made that Mn^{3+} may also be present in black tourmalines. Buergerite spectra show bands due to Fe^{2+} in the near infra-red and red regions, but most features in the visible are swamped by charge-transfer bands. It is concluded that Fe^{3+} is located in the Al^{3+} sites in the spiral chains of black tourmalines, but mainly in the "brucite units" of buergerite.

INTRODUCTION

Earlier published works from these laboratories have dealt with the origin of colour and pleochroism of green and blue tourmalines (Faye, Manning and Nickel, 1968) and pink and brown tourmalines (Manning, 1968*a*). It was suggested that a principal contributor to the colour and pleochroism of green and blue tourmalines was an absorption band in the red end of the spectrum, the band having maximum intensity when the vibration direction of the electric vector of incident light lies in the 001 plane (*i.e.*, E||(001)). The pleochroic band was assigned to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer in the 001 plane. Cations occupying neighbouring octahedral sites in the 001 plane share octahedral-octahedral edges, a geometrical arrangement that implies t_{2g}–t_{2g} orbital overlap. The colour and pleochroism of brown tourmalines was attributed to $Ti^{3+} \rightarrow Ti^{4+}$ interaction in the 001 plane, the band in the blue region at 22000 cm^{-1} having maximum intensity in E||(001) spectra. The colour and pleochroism of pink tourmalines was attributed to Mn^{3+}.

Robbins and Strens (1968) have also assigned the pleochroic 13800 cm^{-1} band in green and blue tourmalines to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer. Wilkins, Farrell and Naiman (1969), on the other hand, attribute the 13800 cm^{-1} band to Fe^{2+} in distorted sites of D_{4h} symmetry.

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The absorption spectrum of a black tourmaline has been studied by Wilkins, Farrell and Naiman (1969). In view of the fact that their interpretations of the spectra of tourmalines generally differ from ours, a study, on our part, of the spectra of black tourmalines seemed desirable.

The absorption spectra of Cr-bearing tourmaline and buergerite are also reported in this work. One of the aims of the current study was to determine in which of the two octahedral sites, spiral chain or trigonal brucite unit, the transition-metal ions are located.

Energy level diagrams for transition-metal ions in cubic fields have been calculated by Tanabe and Sugano (1954), and are reproduced in various reference books, *e.g.*, Cotton (1963).

EXPERIMENTAL DETAILS

The minerals, kindly donated by H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada, came from the following localities: black tourmalines, from Lot 31, Range 1, Villeneuve, Labelle County, Quebec, and from Como, Italy; chrome tourmaline, from Kaavi, Finland; and buergerite, from the type locality at San Luis Potosi, Mexico.

Sections of the minerals cut parallel to the *c*-axis were mounted, polished face to glass, on microscope slides and thinned to the desired thickness. Spectra were obtained using Cary-14 and Beckman DK-2A spectrophotometers.

Extinction coefficients were calculated from the expression

$$\epsilon = \frac{A}{C \cdot l}, \text{ (in units of litres/mole}\cdot\text{cm),}$$

where A is the absorbance of the band, C is the cation concentration in moles per litre, and l is the specimen thickness in cm.

Partial chemical analyses of the minerals are presented in Table 1.

TABLE 1. CHEMICAL ANALYSES OF TOURMALINES, METAL %

	Cr-bearing	Como, black	Villeneuve, black
Fe		5.04	17.24
Cr	2.71		
Mn		0.06	0.57
Ti		0.06	not detected

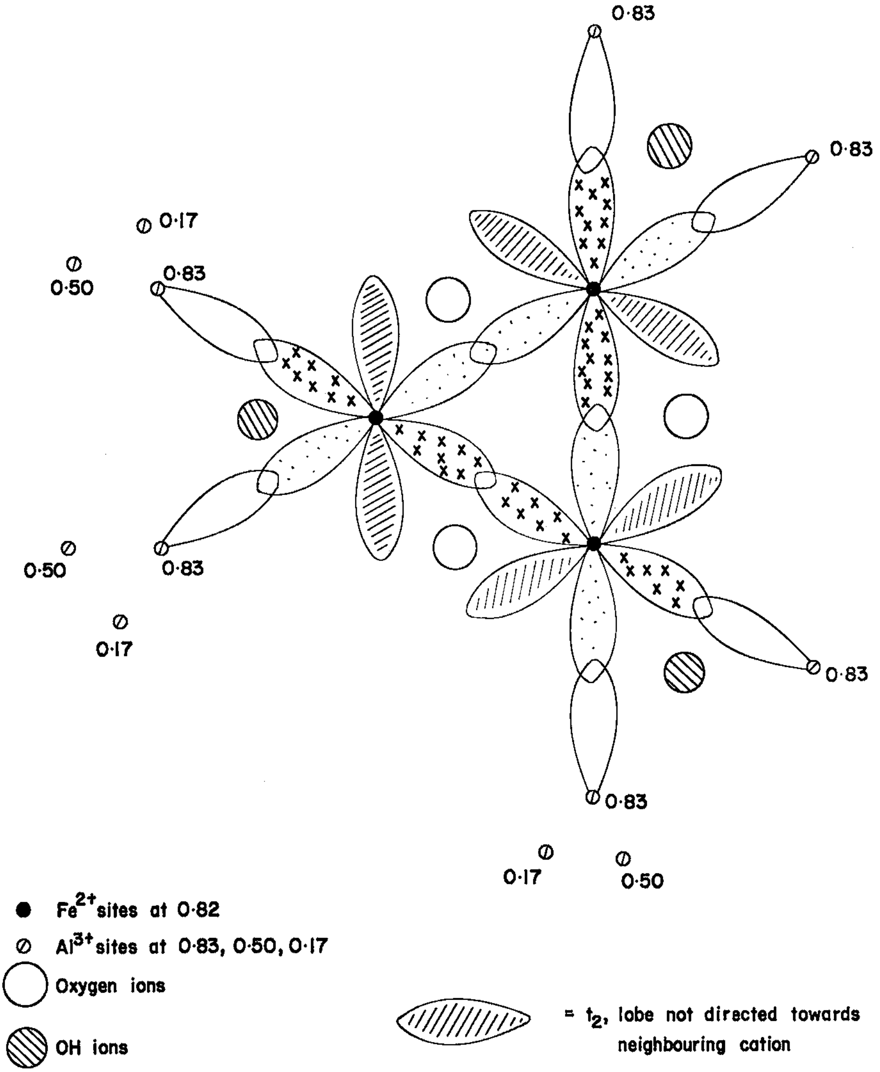

FIG. 1. Diagrammatic representation of the structure of tourmaline projected on (001) showing the relationship between octahedral sites in spiral chains (small crossed circles at heights of 0.83, 0.50 and 0.17) and brucite units (black circles at a height of 0.82) The t_2 orbital lobes lying in the 001 plane are shown as balloon-shaped envelopes for the cations in the trigonal units, and for a few of those in the spiral chains.

DISCUSSION

Structure of Tourmaline

A diagrammatic representation of the structure of tourmaline is shown in Fig. 1. The diagram is based on the structural refinement of dravite (the magnesium tourmaline), by Buerger, Burnham and Peacor (1962). Each Mg^{2+} ion, or, by analogy, each Fe^{2+} ion, is surrounded by four oxygen and two OH ions in a regular octahedron. The octahedra are combined in groups of three, each sharing two of its octahedral edges with its neighbours in the 001 plane. The arrangement is similar to that in the brucite structure, so that these groups can be regarded as "trigonal brucite units". Each of the Fe^{2+}-centred octahedra also shares another two octahedral edges with distorted Al-centred octahedra. Because t_{2g} orbital lobes bisect the octahedral edges, t_{2g}–t_{2g} *d*-orbital overlap occurs in the 001 plane.

Each Al octahedron, in addition to sharing an edge with a Mg octahedron, also shares another two of its edges with Al octahedra diagonally above and below the 001 plane. The projection of the Al^{3+}–Al^{3+} distance on the *c*-axis is larger than that perpendicular to *c*, and $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer between octahedral sites in the spiral chain will be characterised by a pleochroic absorption band in $E\|c$ spectra.

According to Buerger, Burnham and Peacor (1962), the (Mg^{2+}, Fe^{2+})–O distances are in the range 2.02–2.12 Å, with a mean distance of 2.05 Å. The Al^{3+}–O distances in the spiral chain are in the range 1.89–1.98 Å, with a mean distance of 1.93 Å.

It should be stressed that the ionic radii of cations used in this work are empirical (Day and Selbin, 1962) and the sum of the ionic radii may not be related directly to metal–oxygen distances determined by *x*-ray analysis.

Spectra of Cr-bearing tourmaline

Polarized absorption spectra of a section of chromium-bearing tourmaline cut parallel to the *c*-axis are presented in Fig. 2. The two prominent absorption bands at ~17000 cm^{-1} and 24000 cm^{-1} very likely mark the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ in octahedrally-bonded Cr^{3+}. The same two transitions are observed at 17800 cm^{-1} and 2400 cm^{-1} in chromium-bearing pyrope (Manning, 1967*a*), and at 16700 cm^{-1} and 23000 cm^{-1} in uvarovite (Manning, 1968*b*).

The mineral is green in the $E\|(001)$ orientation and yellow-green in the $E \perp (001)$ orientation. The "valley" between the two major bands in the $E \perp (001)$ spectrum (Fig. 2) is shifted toward the red end of the

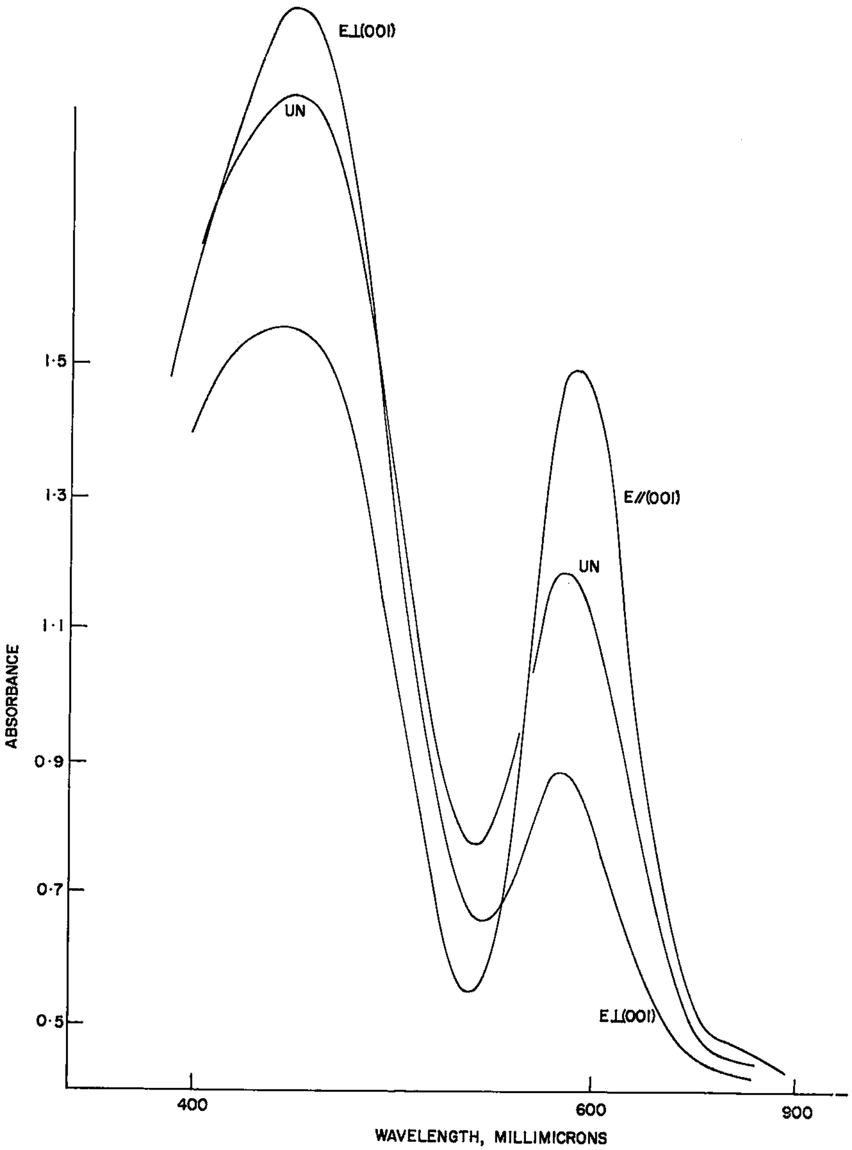

FIG. 2. Polarized (E⊥ (001) and E‖(000) and unpolarized (UN) spectra of Cr-bearing tourmaline, using a specimen 0.005 cm thick.

visible region relative to the "valley" in the E‖(001) spectrum, and this accounts for the greater yellow component in the E ⊥ (001) orientation.

The energy of the ~17000 cm^{-1} band varies by a few hundred cm^{-1} for the different orientations of the electric vector (Fig. 2). This shift in the 24000 cm^{-1} band is also very small. This shows that the splitting of the individual $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ levels is very small and that the Cr^{3+} site is relatively undistorted. The extinction coefficient of the 17000 cm^{-1} band in the unpolarized light spectrum (Fig. 2) is ~50, somewhat greater than for Cr^{3+} in undistorted octahedral sites in pyrope (Manning, 1967*a*).

The sum of the ionic radii (Day and Selbin, 1962) of Cr^{3+} and O^{2-} ions is 2.09 Å (0.69 + 1.40 Å). The substitution of Cr^{3+} for Al^{3+} (0.50 Å) will therefore be accompanied by the expansion of the octahedral site, probably to dimensions between the parent Al–O distance and 2.09 Å. Burns and Strens (1967) have suggested that for an Al–O distance $\geqslant$1.92 Å, the site should be easily expanded to accommodate Fe^{3+} and Cr^{3+}, whereas for Al–O distances <1.92 Å substitution is more difficult and the Fe^{3+}/Cr^{3+} solubility markedly less. Because the magnitude of Δ, the splitting of the e_g and t_{2g} levels, is inversely proportional to the fifth power of the metal–oxygen distance, the "tight site-loose site" boundary corresponds to Δ values of 17400 cm^{-1} and 13700 cm^{-1} for Cr^{3+} and Fe^{3+} respectively (Burns and Strens, 1967).

Because Δ for octahedrally-bonded Cr^{3+} is equal to the energy of the lowest spin-allowed transition $^4A_{2g} \rightarrow {}^4T_{2g}$ (Ballhausen, 1962), it would therefore seem that the ~17000 cm^{-1} bands in Fig. 2 signify a "loose site" for Cr^{3+} in tourmaline. This is consistent with the fact that the mean Al–O distance in dravite is 1.93 Å (Buerger, Burnham and Peacor, 1962). In Table 2 are presented some minerals in which Cr^{3+} is known to substitute for Al^{3+}, together with the mean Al^{3+}–O distances and the Δ-values. Because the magnitude of Δ increases with decreasing metal–oxygen distance, a comparison of the Cr^{3+}–O distances and Δ values in Table 1 suggests that Cr^{3+} substitutes for Al^{3+} in the spiral chain of tourmaline rather than in the larger Mg site.

TABLE 2. DIMENSIONS OF Al–O SITES AND Δ-VALUES FOR SUBSTITUTIONAL Cr^{3+} IN SILICATES

Mineral	Al–O (Å)	Δ (cm^{-1})
Cr_2O_3	1.995 (Newnham and de Haan, 1962)	16670 (Neuhaus, 1960)
uvarovite	1.92 (grossular—Abrahams and Geller, 1958)	16700 (Manning, 1968*b*)
pyrope	1.89 (Zemann and Zemann, 1961)	17800 (Manning, 1967*a*)
muscovite	1.95 (Radoslovich, 1960)	16700 (Faye, 1968)
tourmaline	1.93 (Buerger, Burnham and Peacor, 1962)	17000 (this work)

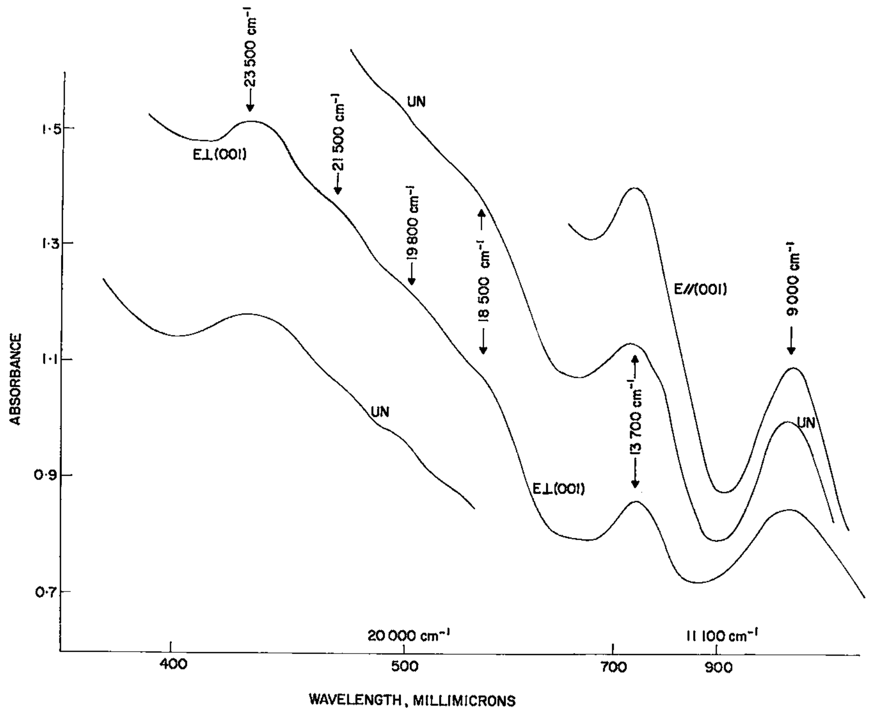

FIG. 3. Polarized (E‖(001) and E⊥ (001)) and unpolarized (UN) spectra of black tourmaline from Villeneuve, Labelle County, Quebec, using a specimen 0.011 cm thick (the two UN curves are the result of using different scale factors for the two ends of the spectrum).

Absorption spectra of black tourmalines

The polarized absorption spectra of two black tourmalines are presented in Figs. 3 and 4. Both spectra show similar absorption features, a major difference being the presence of a strong absorption band at ~18500 cm^{-1} in the Villeneuve spectrum (Fig. 3) that is somewhat weaker in the Como spectrum (Fig. 4). The black tourmaline from Villeneuve contained no detectable amounts of Ti (Table 1), hence the band can likely be accounted for by Fe and Mn. The significance of this band is discussed in detail below.

The absorption bands at 9000 cm^{-1} in both spectra (Figs. 3 and 4) probably mark the $^5T_2 \rightarrow {}^5E(D)$ transition in octahedrally-bonded Fe^{2+}. This assignment agrees with that of Wilkins and co-workers (1969). Ionic radii considerations suggest that Fe^{2+} (radius = 0.76 Å) replaces Mg^{2+} (0.65 Å) in the trigonal brucite units lying in the 001 plane. The 9000 cm^{-1} band is slightly pleochroic in terms of intensity but not energy, with maximum intensity in E‖(001) spectra.

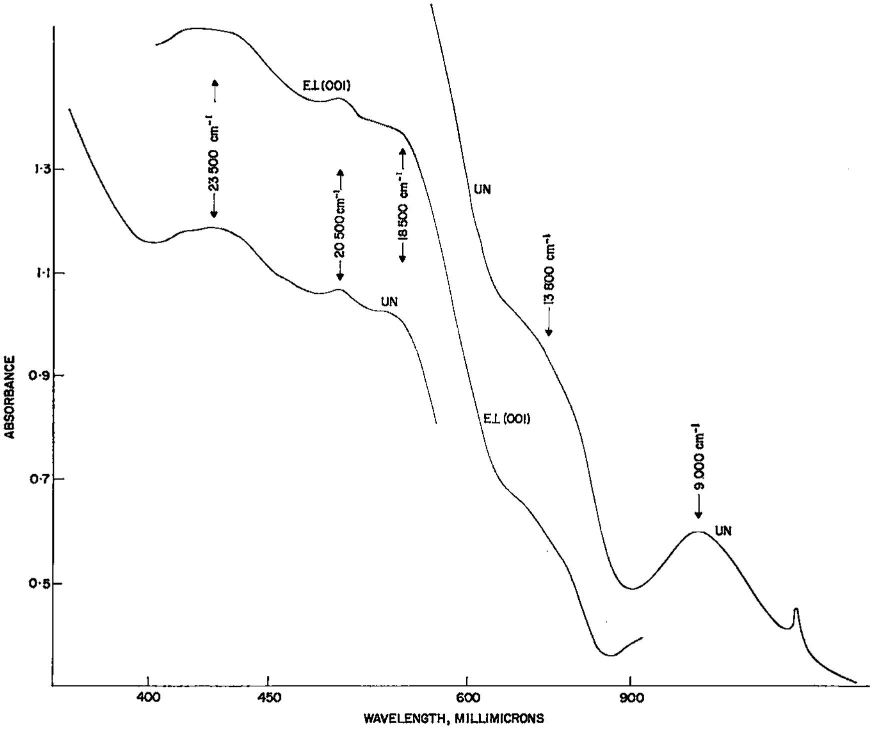

Fig. 4. Polarized (E||(001)) and unpolarized (UN) spectra of black tourmaline from Como, Italy, using a specimen 0.025 cm thick (two different scale factors were used for the unpolarized spectrum).

The absorption band at 13800 cm^{-1} in the spectra of the two tourmalines (Figs. 3 and 4) is markedly pleochroic, with minimum intensity in E ⊥ (001). The E||(001) spectrum in Fig. 3 was too intense to be resolved, but the polarization properties of the band are easily evident. The 13800 cm^{-1} absorptions in black tourmalines are equivalent to the 13800 cm^{-1} bands in the spectra of green and blue tourmalines studied earlier (Faye, Manning and Nickel, 1968) which were assigned to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer via *d*-orbital overlap in the 001 plane.

The absorption bands in the blue end of the spectra in Figs. 3 and 4 are probably due to the presence of one, or more, of Fe^{3+}, Mn^{2+} or Mn^{3+}. Black tourmalines often contain significant amounts of Fe^{3+}, and this is seemingly confirmed by the presence of the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band. The Mn contents of the two black tourmalines (Table 1) are very different, the Villeneuve sample containing 0.57% Mn and the Como specimen 0.058%. The total Fe and Mn analyses, unfortunately, do not give any indication of the relative amounts of the two main valence states in the two specimens.

The band at 23500 cm^{-1} is much better resolved in the Como spectrum (Fig. 4) than in the Villeneuve spectrum (Fig. 3). Because the latter specimen contains considerably more Mn, and because Mn^{2+} absorbs weakly at 24500 cm^{-1} and 23000 cm^{-1} (Manning, 1968*c*), it is conceivable that the broadness of the 23500 cm^{-1} band is due to the transitions $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ and $^6A_1 \rightarrow {}^4T_2(G)$ in Mn^{2+}. The Villeneuve spectrum also shows a small well-defined band at 20500 cm^{-1} that could mark the transition $^6A_1 \rightarrow {}^4T_1(G)$ in Mn^{2+} ions located in the trigonal brucite sites. The 23500 cm^{-1} band in black tourmalines could then mark the field-independent transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in Fe^{3+}. The band is not as sharp as in andradites (Manning, 1967*b*), but the band is not very sharp in grossular spectra either (Manning, 1968*b*).

If the spectral features in the green and blue regions of Figs. 3 and 4 are assigned in the main to Fe^{3+}, then the assignment of the 13800 cm^{-1} band to $Fe^{2+} \rightarrow Fe^{3+}$ electron-hopping must be considered doubtful. Absorption bands due to Fe^{3+} were not observed in the spectra of green and blue tourmalines (Faye, Manning and Nickel, 1968) and yet the relative intensities of the 9000 cm^{-1} and 13800 cm^{-1} bands in Figs. 3 and 4 are very similar to the relative intensities of the same bands in green and blue tourmalines. The greater the Fe^{3+} concentration, the greater the probability of $Fe^{2+} \rightarrow Fe^{3+}$ interaction and the greater the intensity of the 13800 cm^{-1} band relative to the 9000 cm^{-1} band. The fact that 13800 cm^{-1} band does not extinguish in the $E \perp (001)$ spectra might also be taken as evidence that the band belongs to Fe^{2+}, although it is possible that the band in the $E \perp (001)$ orientation reflects $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer parallel to *c*.

The substitution of Fe^{3+} for Al^{3+} is quite commonplace in silicate minerals. The sum of the radii of Fe^{3+} and O^{2-} is 2.04 Å; therefore, as for Cr^{3+}, Fe^{3+} substitution will cause the expansion of the Al^{3+} site. In Table 3 are presented some minerals in which Fe^{3+} is known to substitute for Al^{3+}, together with the dimensions of the Al^{3+} sites. Also included for convenient references are the energies of the $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition in Fe^{3+}. It would seem, from the fact that many of the minerals contain appreciable amounts of Fe^{3+}, that Fe^{3+} will substitute for Al^{3+} readily if the Al–O length > 1.92 Å. In vesuvianite, Fe^{3+} is located mainly in the Al^{3+} site (Al–O = 1.95 Å) rather than in the larger Mg (Mg–O = 2.05 Å) site (Manning, 1968*d*). Consequently, it seems reasonable to suggest that Fe^{3+} is located in the spiral chain (Al^{3+} sites) of tourmaline, and presumably in all varieties (except buergerite, see below). Considerations

TABLE 3. AVERAGE Al–O DISTANCES AND ENERGIES OF $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ TRANSITION IN SUBSTITUTIONAL Fe^{3+} IN SILICATES

Mineral	% Fe^{3+}	Al–O (Å)	E (cm^{-1})	Reference
Almandine	1	1.89	21800	Manning (1967*a*)
Vesuvianite	2	1.95	21600	Manning (1968*d*)
Epidote	~5	1.94	22000	Burns and Strens (1967)
Titanaugite[1]	3.5	~1.99	22000	Manning (1968*e*)
Andradite	20	1.92	22700	Manning (1967*b*)
Muscovite	6	1.95	22600	Faye (1968)
Kyanite	0.9	1.89	22900	White and White (1967)
Riebeckite[2]	10	~2.00	23000	Manning (1968*e*)
Pink tourmaline	1	1.93	22000	Manning (1968*a*)
Blacktourmaline	1–10	1.93	23500	This work

[1] Fe substitutes for Mg^{2+}.
[2] Fe^{3+} principal constituent of M_2 site.

of ionic radii further suggest that Ti^{3+} (0.76 Å) and Ti^{4+} (0.67 Å) are located in the brucite units and spiral chain, respectively.

Wilkins, Farrell and Naiman (1969) assigned the 9200 cm^{-1} and 13800 cm^{-1} bands in black tourmalines to electronic transitions in Fe^{2+}, split in a field of D_{4h} symmetry. The 9000 cm^{-1} and 13800 cm^{-1} bands in black tourmalines are surprisingly widely separated in view of the fact that splittings for other transition-metal ions seem negligible (*e.g.*, Cr^{3+}). Wilkins and co-workers (1969) attributed bands around 20000 cm^{-1} to Fe^{3+} in both spiral chain and brucite units.

Absorption spectra of buergerite

Polarized absorption spectra of buergerite, the trivalent iron tourmaline, are presented in Fig. 5. Buergerite is dark-brown in E‖(001) spectra and yellow in E ⊥ (001). Chemical analysis of the buergerite for total Fe and Mn agree well with analyses reported by Donnay, Ingamells and Mason (1966) of a buergerite from the same locality. The buergerite has the composition:

$$(Na_{2.5}K_{0.05}Ca_{0.4})(Fe^{3+}_{6.9}Fe^{2+}_{0.55}Mn_{0.06}Ti_{0.2}Al_{0.8}Mg_{0.1})Al_{18}B_{9.3})$$
$$(Si_{17.5}B_{0.5})(O_{88.8}OH_{1.2})(Fe_{3.05}OH_{0.2}).$$

Donnay, Ingamells and Mason (1966) assigned Fe^{2+} and Fe^{3+} to the trigonal brucite units, by analogy with the structure of schorl.

The 7700 cm^{-1} band in buergerite spectra (Fig. 5) probably marks the $^5T_2 \rightarrow {}^5E(D)$ transition in octahedrally-bonded Fe^{2+}. The extinction coefficient is 1 litre/mole·cm, in reasonable agreement with the intensity ($\epsilon \sim 4$) of the corresponding Fe^{2+} bands in green and blue tourmaline (Faye, Manning and Nickel, 1968). The 7700 cm^{-1} band is weakly pleochroic in terms of intensity, in keeping with the pleochroism of Fe^{2+}

bands in green and blue tourmalines. The energy of the 7700 cm^{-1} band is considerably lower than the energies of the corresponding bands in green, blue and black tourmalines (this work). The Fe^{3+} ions in buergerite may polarize the anions in such a way as to reduce the strength of the ligand field around Fe^{2+} thus lowering the energy of the $^5T_2 \rightarrow {}^5E(D)$ transition.

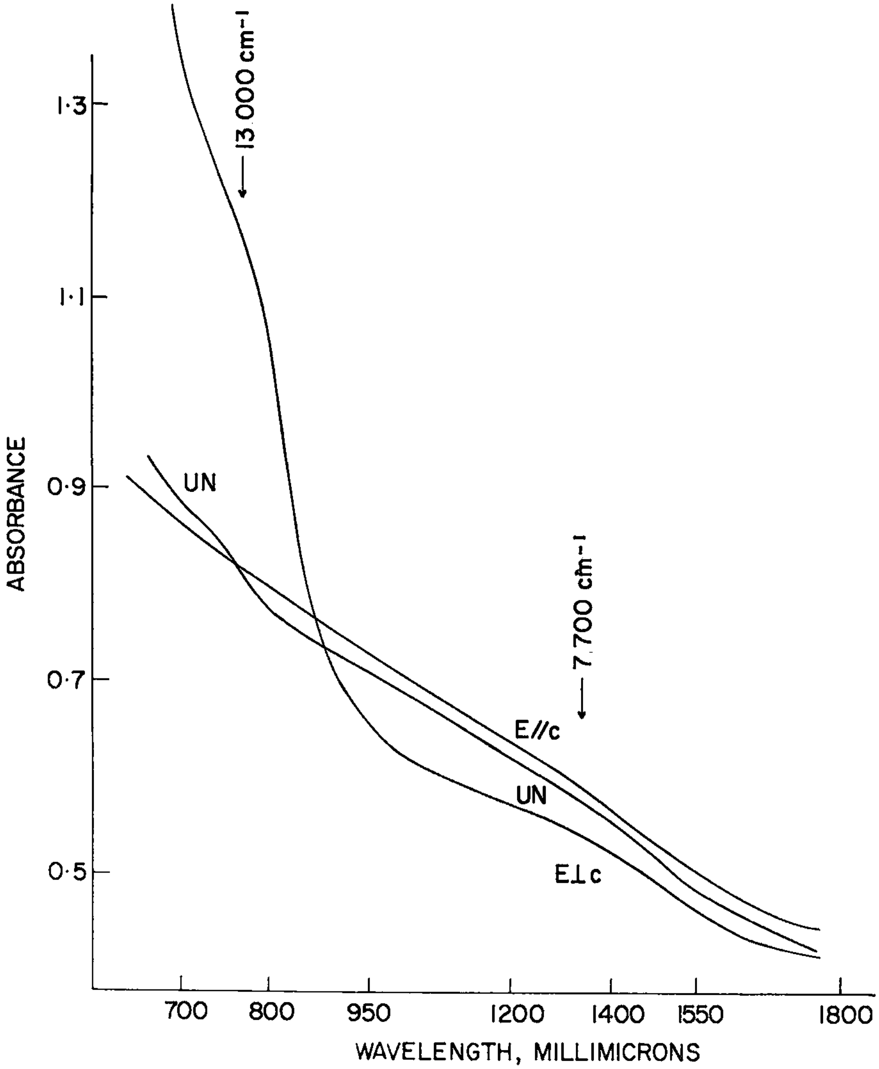

FIG. 5. Polarized (E‖*c* and E⊥ *c*) and unpolarized spectra of buergerite, using a specimen 0.002 cm thick.

The 13000 cm^{-1} band (Fig. 5) with maximum intensity in E‖(001) spectra is analogous to the 13800 cm^{-1} bands in green, blue and black tourmalines. Its intensity relative to that of the 7700 cm^{-1} Fe^{2+} band is similar to that for the other tourmalines, suggesting that the 13000 cm^{-1} band is not an $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band. The Fe^{3+} concentration in buergerite is ten times that of Fe^{2+}, compared with more-or-less the inverse ratio in green and blue tourmalines.

The cell dimensions of buergerite and schorl are presented in Table 4. The smaller *a* dimension of buergerite is consistent with the replacement of (Mg^{2+}, Fe^{2+}) in schorl by the smaller Fe^{3+} ions in buergerite. The *c*-dimension would be expected to be influenced primarily by the occupancy of the octahedral sites in the spiral chains that run parallel to the *c*-axis: the slightly larger *c*-dimension of buergerite could therefore indicate some Fe^{3+} (0.67 Å) substitution for Al^{3+} (0.50 Å) in the spiral chain of buergerite. The spectra and cell dimensions of buergerite are consistent with most of the Fe^{3+}, and essentially all of the Fe^{2+}, occupying sites in the trigonal brucite units, but with some Fe^{3+} in the spiral chain.

TABLE 4. CELL DIMENSIONS OF BUERGERITE AND SCHORL IN Å UNITS

	Buergerite (Donnay, Ingamells & Mason, 1966)	Schorl (Epprecht, 1953)
a	15.873	16.032
c	7.187	7.149

No Fe^{3+} bands were identified in buergerite spectra, probably because of the weakness of Fe^{3+} bands and the intensity of the absorption edge. Bearing in mind the possible geochemical correlation between Fe^{3+} and Mn^{3+} observed in pink tourmalines (Manning, 1968*a*), it is conceivable that Mn is present as Mn^{3+} in buergerite: a weak absorption at 20000 cm^{-1} is observed in buergerite spectra (not shown in Fig. 5), which could be the $^5E_g \rightarrow {}^5T_{2g}$ transition in Mn^{3+} (Manning, 1968*a*). The prominent absorption at approximately 18500 cm^{-1} in the Villeneuve spectrum (Fig. 3) could be due Mn^{3+}.

The author has discussed the origin of the 13800 cm^{-1} band in tourmalines with G. H. Faye of the Mines Branch, who has additional information on the splitting of Fe^{2+} bands in a number of silicates including tourmaline. He also believes that the 13800 cm^{-1} band could be a Fe^{2+} band.

CONCLUSIONS

Absorption spectra of green, Cr-bearing tourmaline show that the principal chromophore, Cr^{3+}, is located in the octahedral sites in the spiral chain. The colour of black tourmaline is due to transitions within Fe^{2+} and Fe^{3+}, and to transitions within another ion, possibly Mn^{3+}. Fe^{2+} absorbs at 9000 cm^{-1} and 13800 cm^{-1}. Buergerite shows absorptions at 7700 cm^{-1} and at 13000 cm^{-1} due to Fe^{2+}. The Fe^{3+} ions are located mainly in the spiral-chain sites in tourmalines except for buergerite, where they are located chiefly in the "trigonal brucite units". Fe^{2+} and Mn ions are mainly in the brucite-type sites in all tourmalines.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. R. Craig, of the Inorganic Chemistry Subdivision, for performing the analyses, and Dr. E. H. Nickel and Mr. G. H. Faye for many useful discussions. The author also thanks Dr. R. W. T. Wilkins for a preprint of the paper by Wilkins, Farrell and Naiman.

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Manuscript received November 1, 1968; emended May 20, 1969

COBALT–GOWGANDA ISSUE

A Cobalt–Gowganda issue is currently being prepared by Dr. W. Petruk, Mines Branch, and Dr. J. L. Jambor, Geological Survey of Canada. This issue will be edited by the co-authors and others in the Department of Energy, Mines and Resources, Canada, and will be published by the Canadian Mineralogist as a special issue about 1970. Information on research being conducted on the Cobalt–Gowganda ores, and copies of manuscripts that could be included in this issue are invited. Please forward all information and manuscripts to Dr. W. Petruk, Mines Branch, 555 Booth Street, Ottawa 4, Ontario.