EFFECT OF SECOND-NEAREST-NEIGHBOUR INTERACTION ON Mn$^{3+}$ ABSORPTION IN PINK AND BLACK TOURMALINES

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ABSTRACT

Optical absorption studies demonstrate that the extinction coefficients of bands marking the transition $^5E_g \rightarrow ^6T_{2g}$ in octahedral-Mn$^{3+}$ are at least an order of magnitude greater in black tourmalines than in pink. Ultraviolet charge-transfer absorption sweeping into the visible-region is more prominent in black tourmalines. It is proposed that the stronger absorption in black tourmalines is due to distortion of Mn$^{3+}$ octahedra brought about by substitution of adjacent Si$^{4+}$ ions by Fe$^{3+}$ and Al$^{3+}$. Two relatively-sharp bands at ~20000 cm$^{-1}$ (500nm) in spectra of black tourmalines have been assigned to transitions to the $^4T_1$ and $^4T_2$ levels in tetrahedral-Fe$^{3+}$.

INTRODUCTION

Previous studies of the optical spectra of pink (rubellite) and black (schorl) tourmalines (Manning 1969a, 1969b) have suggested that the principal absorbing cation in both varieties is octahedral-Mn$^{3+}$, in concentrations of ~0.1-0.5%. The essential difference in light-absorption properties giving rise to the pink and black colours is in the intensity of the Mn$^{3+}$ d-d and charge-transfer bands. In the current work a more detailed study is made of the spectra, including accurate curve-resolution, in order to determine the structural implications of the differences in colour. Earlier studies (Manning 1969a) suggested that Cr$^{3+}$ (ionic radius 0.63 Å) and Fe$^{3+}$ (0.64Å) ions prefer the octahedral Al$^{3+}$ sites rather than the octahedral sites of the brucite units. It is likely that this is also the case for Mn$^{3+}$ (0.66 Å).

The crystal structures of a rubellite and a dravite have been refined by Buerger, Burnham & Peacor (1962). Each Al$^{3+}$ ion is surrounded by 5 oxygens and one OH group. Two of the oxygens, in trans positions, are bonded to two B atoms of BO$_3$ trigonal units. The three remaining oxygens are bonded to tetrahedral-Si$^{4+}$ ions.

EXPERIMENTAL DETAILS

The measurement of absorption spectra has been described in an earlier work (Manning 1969a). Spectra of two other black tourmalines were
measured, in addition to the two from Villeneuve and Como reported earlier; all showed similar absorption features.

Extinction coefficients were calculated from the expression

$$\varepsilon = \frac{A}{C \cdot l},$$  \hspace{0.5cm} (in units of litres/mole-cm),

Fig. 1. Optical spectrum of a section of black tourmaline, from Villeneuve, Quebec, cut parallel to the c-axis and using unpolarized light. Sample thickness = 0.011 cm.

Fig. 2. Unpolarized-light spectrum of a parallel-to-c section of a black tourmaline from Como, Italy. Sample thickness = 0.028 cm.
where $A$ is the absorbance of the band, $C$ is the cation concentration in moles/litre, and $l$ is the specimen thickness in cm.

**Discussion**

Resolved spectra of two black tourmalines are shown in Figures 1 and 2; both spectra show similar absorption features. The original unresolved spectra have been presented earlier (Manning 1969a). I assigned the two near-infrared bands (at $\sim 9000$ and $\sim 13500$ cm$^{-1}$) to octahedral-Fe$^{2+}$, the major visible-region band (at 18400 cm$^{-1}$) to the $6E \rightarrow 5T_{2g}$ transition in octahedral-Mn$^{3+}$, and the $\sim 22700$ cm$^{-1}$ band (broadened by Mn$^{2+}$ absorptions commonly observed at 23000-24000 cm$^{-1}$) to the field-independent transition $6A_1 \rightarrow 4A_1^4E(G)$ in octahedral-Fe$^{3+}$. Curve resolution (Figs. 1 and 2) shows, however, that the 22700 cm$^{-1}$ bands are too broad (half-width 2400 cm$^{-1}$) to characterize a field-independent transition.

It seems more reasonable assigning the 18400 cm$^{-1}$ and 22700 cm$^{-1}$ bands to components of the transition $6E \rightarrow 5T_{2g}$ in octahedral-Mn$^{3+}$. Mn$^{3+}$ ions are stabilized in tetragonally-distorted octahedral sites, and two absorption bands at $\sim 2000$ cm$^{-1}$ are observed for Mn$^{3+}$ in a variety of oxygen-ligand fields (Dingle 1966). Similar absorption spectra have been observed for Mn$^{3+}$ ions in epidote (bands at 18250 and 22000 cm$^{-1}$; Burns & Strens 1967), manganophyllite (19050 and 21400 cm$^{-1}$; Burns 1970) and pink tourmaline (19200 and $\sim 21400$ cm$^{-1}$; Manning 1969b). Calculated $\varepsilon$-values for the 18400 cm$^{-1}$ band in black tourmalines are in the range 180-300 assuming that all Mn is Mn$^{3+}$.

A resolved spectrum of a pink tourmaline is given in Figure 3. All bands are due to Mn$^{3+}$ (Table 1). Dingle (1966) has suggested that bands of Mn$^{3+}$ in oxygen fields in the energy range 5000-15000 cm$^{-1}$ are charge-transfer bands. The two sharp peaks at $\sim 22000$ cm$^{-1}$ were originally assigned to the $6A_1 \rightarrow 4A_1^4E(G)$ transition in octahedral-Fe$^{3+}$ (Manning 1969b). However, the pink tourmaline studied here contained $< 0.01\%$ Fe, based on which $\varepsilon > 10$. This $\varepsilon$-value seems too high, especially in view of the fact that intense charge-transfer bands are absent (Manning & Townsend 1970). Hence the sharp peaks may mark spin-forbidden field-independent transitions in Mn$^{3+}$ (see the energy-level diagrams of Berkes (1968)). Most significantly, $\varepsilon_{18200} \sim 15$, assuming that all Mn is Mn$^{3+}$, which is an order of magnitude smaller than for the 18400 cm$^{-1}$ band in black tourmalines. The «colour» of black tourmalines is due mainly to strong Mn$^{3+}d-d$ bands superimposed on the low-energy wing of intense charge-transfer absorption centred in the ultraviolet. I propose that in black tour-
Fig. 3. Unpolarized-light spectrum of a basal section of the pink core of a "watermelon" tourmaline. Thickness = 0.32 cm.

Table 1. Electron-Microprobe Analyses of Pink and Black Tourmalines

<table>
<thead>
<tr>
<th>Metal, %</th>
<th>Villeneuve (black) *</th>
<th>Como (black)</th>
<th>Pink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>11.78</td>
<td>5.04</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mn</td>
<td>0.57</td>
<td>0.06</td>
<td>0.20</td>
</tr>
<tr>
<td>Ti</td>
<td>n.d.</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>17.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Also contains: Na 1.72% ; Ca 0.11% ; Mg 0.39% ; Si 15.09%.
N.d. = not detected, generally < 0.01%.
maline the \( \text{Mn}^{3+} \) transition borrows intensity from charge-transfer transitions (e.g. \( \text{O}^{2-}-2p \rightarrow \text{Mn}^{3+}3d \)) through crystal-field mixing of odd-parity charge-transfer states with even-parity \( d \) states.

Tourmalines containing 3-5% Fe are usually blue or green (Deer, Howie & Zussman 1962; Faye et al. 1968), the principal colour centres being \( \text{Fe}^{2+}d-d \) bands in the 700 nm region. Hence, it is unlikely that the "colour" of black tourmalines is due to \( \text{Fe}^{2+} \). Spectra of black tourmalines (Figs. 1 and 2) show two relatively-sharp absorptions (half-widths 900 cm\(^{-1}\)) at 20100 and \( \sim 21200 \) cm\(^{-1}\) and another two at \( \sim 24000 \) cm\(^{-1}\), which could mark the transitions \( ^6A_1 \rightarrow ^4T_1(G), \rightarrow ^4T_2(G) \), and \( \rightarrow ^4A_1^4E(G) \) in tetrahedral-\( \text{Fe}^{3+} \) respectively. Two relatively-sharp bands at \( \sim 20000 \) cm\(^{-1}\) have been observed in spectra of \( \text{Fe}^{3+} \) in tetrahedral sites in orthoclase (Faye 1969; Manning 1970), phlogopite (Faye & Hogarth 1969), silicate glass (Kurkjian & Sigety 1968), and also in several garnets (Manning 1972). Two bands of half width 900 cm\(^{-1}\) in spectra of some garnets (Manning 1972) at \( \sim 24000 \) cm\(^{-1}\) have been assigned to tetrahedral \( \text{Fe}^{3+} \). The current assignments are reasonable based on values of \( D_0 \sim 600 \) cm\(^{-1}\) and Racah parameters \( B = 600 \) cm\(^{-1}\) and \( C = 3600 \) cm\(^{-1}\). Black tourmalines are often Si-deficient (Deer, Howie & Zussman 1962). Competition for these tetrahedral sites will likely be between \( \text{Al}^{3+} \) and \( \text{Fe}^{3+} \), both of which are known to occur in tetrahedral coordination in minerals. Hartman (1969) used crystallographic arguments to suggest that the order of substitution of cations into Si sites in garnets is \( \text{Al}^{3+} > \text{Fe}^{3+} > \text{Ti}^{4+} \). It seems reasonable to suggest therefore that substitution of tetrahedral \( \text{Si}^{4+} \) by less-covalent \( \text{Al}^{3+} \) and \( \text{Fe}^{3+} \) ions destroys the inversion symmetry at adjacent octahedral sites by distorting the oxygen octahedra. Lengths and covalencies of \( \text{Mn}^{3+} \) bonds to oxygens of substituted tetrahedra will be different in pink and black tourmalines. Oxygen \( \rightarrow \) metal\(^{8+} \) charge-transfer will likely intensify. A similar mechanism has been invoked to explain the intense \( \text{Fe}^{3+} \) charge-transfer and crystal-field bands in the black garnet schorlomite, in which substitution of adjacent \( \text{Si}^{4+} \) by other cations occurs (Manning & Townsend 1970). Absorption in black tourmalines is greatest in spectra where the vibration direction of incident light is perpendicular to the c-axis (Manning 1969a). The projection of \( \text{Mn}^{3+} \rightarrow \text{O} \) bonds is greatest on a plane perpendicular to c.

It is conceivable that the higher \( \epsilon \)-values for \( \text{Mn}^{3+}d-d \) bands in black tourmalines is due to a higher \( \text{Mn}^{3+}:\text{Mn}^{2+} \) ratio. However, cell-dimensions of schorls are greater than of elbaits (Deer, Howie & Zussman 1962), suggesting that the solubility of the larger \( \text{Mn}^{2+} \) ion is likely to be greater in schorl.
The Si deficiency in black tourmalines (Deer, Howie & Zussman 1962) does not seem to exceed 0.3 atoms out of 6. There are relatively 6 available Al sites, hence if the distribution coefficient between octahedral and tetrahedral sites is equal for \( \text{Al}^{3+} \) and \( \text{Fe}^{3+} \), then the expected ratio of concentrations of octahedral-\( \text{Fe}^{3+} \) : tetrahedral-\( \text{Fe}^{3+} \) is \( \sim 20 \). The \( \varepsilon \) value of the easily-recognizable transition \( ^6A_1 \rightarrow ^4A_1^*E(G) \) in \( \text{Fe}^{3+} \) in regular octahedral sites in garnets is 1-2 (Manning 1967). No absorption bands of octahedral-\( \text{Fe}^{3+} \) are evident in Figures 1 and 2, hence the necessary \( \varepsilon \)-value for the tetrahedral-\( \text{Fe}^{3+} \) band at 20100 cm\(^{-1}\) to be stronger than octahedral-\( \text{Fe}^{3+} \) bands must be at least, say, 30. Since a sharp octahedral-\( \text{Fe}^{3+} \) band of intensity 0.04 units would be easily observed, e.g. in Figure 1, the necessary \( \varepsilon \)-value becomes \( \sim 60 \). Furthermore, in the same way that the octahedral-\( \text{Mn}^{3+} \) transitions gain intensity from charge-transfer processes, so also will transitions in octahedral-\( \text{Fe}^{3+} \), possibly by an order of magnitude, as has been observed in spectra of schorlomite garnet (Manning & Townsend 1970). I feel, therefore, that the necessary \( \varepsilon \)-values are beyond acceptable limits for spin-forbidden bands of \( \text{Fe}^{3+} \). Hence, the distribution coefficient (concentration of tetrahedral cation/concentration of octahedral cation) must be considerably greater for \( \text{Fe}^{3+} \) than for \( \text{Al}^{3+} \). This reflects greater covalency of \( \text{Fe}^{3+} \)-oxygen bonds. If \( \text{Fe}^{3+} \) ions occupy 0.2 of the 6 Si sites, the implied \( \varepsilon \)-value for the 20100 cm\(^{-1}\) tetrahedral-\( \text{Fe}^{3+} \) band is \( \sim 10 \).

The \( \varepsilon \)-value of the 22700 cm\(^{-1}\) band in andradites (1-2) is considerably smaller than that observed (\( \sim 500 \)) for the corresponding band in synthetic \( \text{Gd}_5\text{Fe}_3\text{O}_{12} \) garnet (Levenson & Sawatzky 1969). Absorption by \( \text{Fe}^{3+} \) ions is considerably more intense in \( \text{Fe}_2\text{O}_3 \) than in silicates. This indicates that \( \text{O}^{2-} \rightarrow \text{Fe}^{3+} \) charge-transfer is more efficient in oxides, probably for the reason that Si-O covalency in silicates reduces the effective charge on adjacent oxygens. It would appear that oxygens of Si-substituted tetrahedra in black tourmalines have \( \text{O}^{2-} \rightarrow \text{M}^{3+} \) charge-transfer properties similar to those of oxides.

The spectra reported in this article are considerably reduced in size from those actually measured, and for this reason the weak peaks marking the two \( \text{Fe}^{3+} \) bands at 20100 cm\(^{-1}\) and 21300 cm\(^{-1}\) are difficult to see (Figs. 1 and 2). There are definitely two peaks at 20100 cm\(^{-1}\) and 21300 cm\(^{-1}\) that can be seen by eye in the original spectra, and the curve-resolver does resolve two bands of similar half-widths and relative intensities in spectra of 4 black tourmalines. Estimating the background absorption is not critical in this part of the spectrum as it is at \( \sim 24000 \) cm\(^{-1}\). The \( \text{Mn}^{3+} \) spectra are different in pink and black tourmalines, in the
separation and also the relative intensities of the two component \( d-d \) bands, but this may be a manifestation of the greater distortion of the Mn\(^{3+}\) polyhedra in black tourmalines.

**References**


Manning, P.G. (1967) : The optical absorption spectra of some andradites and the identification of \( \epsilon A_1 \rightarrow \epsilon A_1^*E(G) \) transition in octahedrally-bonded Fe\(^{3+}\). *Can. J. Earth Sci.* 4, 1039.


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