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 $^5E_g \rightarrow {}^5T_{2g}$ 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

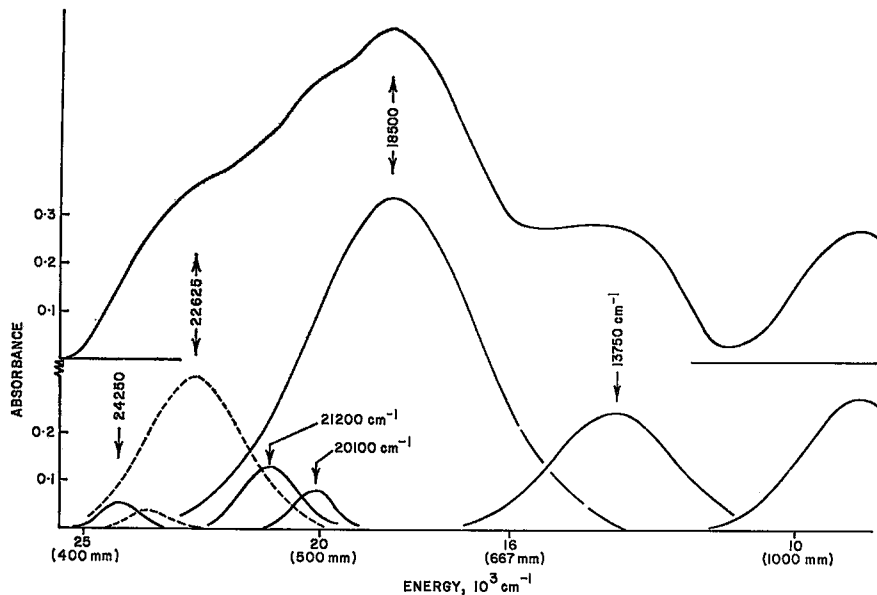$$\varepsilon = \frac{A}{C.l} , \text{ (in units of litres/mole-cm)},$$

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.
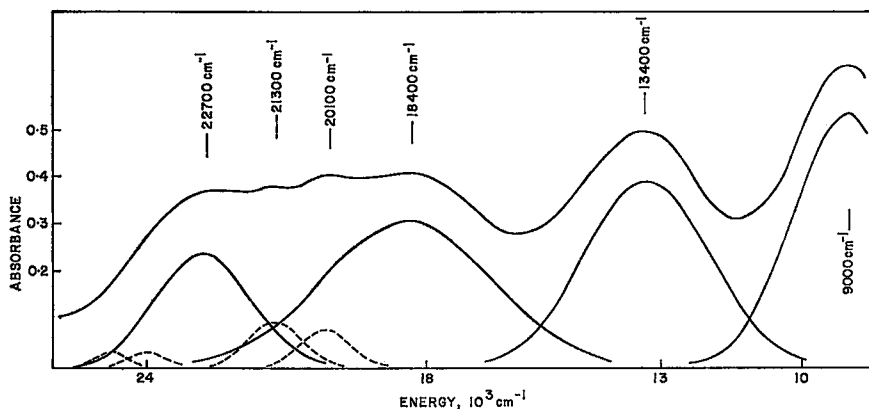

Fig. 2. Unpolarized-light spectrum of a parallel-to-c section of a black tourmaline from Como, Italy. Sample thickness = 0.028 cm.

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 ~ 9000 and ~ 13500 cm⁻¹) to octahedral-Fe^{2+}, the major visible-region band (at 18400 cm⁻¹) to the $^5E \to {}^5T_{2g}$ transition in octahedral-Mn^{3+}, and the ~ 22700 cm⁻¹ band (broadened by Mn^{2+} absorptions commonly observed at 23000-24000 cm⁻¹) to the field-independent transition $^6A_1 \to {}^4A_1{}^4E(G)$ 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 $^5E_g \to {}^5T_{2g}$ in octahedral-Mn^{3+}. Mn^{3+} ions are stabilized in tetragonally-distorted octahedral sites, and two absorption bands at ~ 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 ~ 21400 cm⁻¹ ; Manning 1969b). Calculated ε-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 ~ 22000 cm⁻¹ were originally assigned to the $^6A_1 \to {}^4A_1 {}^4E(G)$ transition in octahedral-Fe^{3+} (Manning 1969b). However, the pink tourmaline studied here contained < 0.01% Fe, based on which ε > 10. This ε-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, ε_{19200} ~ 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-
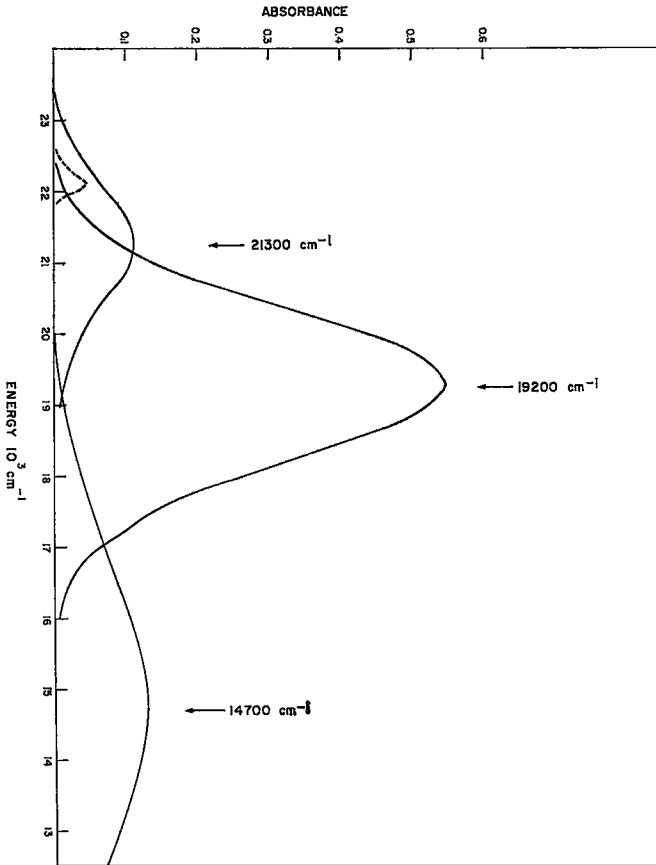
Fig. 3. Unpolarized-light spectrum of a basal section of the pink core of a "watermelon" tourmaline. Thickness = 0.32 cm.

TABLE 1. ELECTRON-MICROPROBE ANALYSES OF PINK AND BLACK TOURMALINES

Metal, %	Villeneuve (black) *	Como (black)	Pink
Fe	11.78	5.04	n.d.
Mn	0.57	0.06	0.20
Ti	n.d.	0.06	
Al	17.19		

* Also contains : Na 1.72% ; Ca 0.11% ; Mg 0.39% ;
Si 15.09%.
N.d. = not detected, generally < 0.01%.

maline the $Mn^{3+} \, ^5E_g \rightarrow \, ^5T_{2g}$ transition borrows intensity from charge-transfer transitions (e.g. $O^{2-}2p \rightarrow Mn^{3+}3d$) 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 $Fe^{2+}d$-d bands in the 700 nm region. Hence, it is unlikely that the « colour » of black tourmalines is due to Fe^{2+}. Spectra of black tourmalines (Figs. 1 and 2) show two relatively-sharp absorptions (half-widths 900 cm^{-1}) at 20100 and ~ 21200 cm^{-1} and another two at ~ 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-Fe^{3+} respectively. Two relatively-sharp bands at ~ 20000 cm^{-1} have been observed in spectra of Fe^{+3} in tetra-hedral 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 ~ 24000 cm^{-1} have been assigned to tetrahedral Fe^{3+}. The current assignments are reasonable based on values of D_q ~ 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 Al^{3+} and 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 $Al^{3+} > Fe^{3+} > Ti^{4+}$. It seems reasonable to suggest therefore that substitution of tetrahedral Si^{4+} by less-covalent Al^{3+} and Fe^{3+} ions destroys the in-version symmetry at adjacent octahedral sites by distorting the oxygen octa-hedra. Lengths and covalencies of Mn^{3+} bonds to oxygens of substituted tetrahedra will be different in pink and black tourmalines. Oxygen $\rightarrow$ metal^{3+} charge-transfer will likely intensify. A similar mechanism has been invoked to explain the intense Fe^{3+} charge-transfer and crystal-field bands in the black garnet schorlomite, in which substitution of adjacent 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 projec-tion of $Mn^{3+} - O$ bonds is greatest on a plane perpendicular to c.

It is conceivable that the higher ε-values for $Mn^{3+}d$-d bands in black tourmalines is due to a higher $Mn^{3+}:Mn^{2+}$ ratio. However, cell-dimensions of schorls are greater than of elbaites (Deer, Howie & Zussman 1962), suggesting that the solubility of the larger 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 Al^{3+} and Fe^{3+}, then the expected ratio of concentrations of octahedral-Fe^{3+} : tetrahedral-Fe^{3+} is ~ 20. The ε value of the easily-recognizable transition $^6A_1 \to {}^4A_1{}^4E(G)$ in Fe^{3+} in regular octahedral sites in garnets is 1-2 (Manning 1967). No absorption bands of octahedral-Fe^{3+} are evident in Figures 1 and 2, hence the necessary ε-value for the tetrahedral-Fe^{3+} band at 20100 cm^{-1} to be stronger than octahedral-Fe^{3+} bands must be at least, say, 30. Since a sharp octahedral-Fe^{3+} band of intensity 0.04 units would be easily observed, e.g. in Figure 1, the necessary ε-value becomes ~ 60. Furthermore, in the same way that the octahedral-Mn^{3+} transitions gain intensity from charge-transfer processes, so also will transitions in octahedral-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 ε-values are beyond acceptable limits for spin-forbidden bands of Fe^{3+}. Hence, the distribution coefficient (concentration of tetrahedral cation/concentration of octahedral cation) must be considerably greater for Fe^{3+} than for Al^{3+}. This reflects greater covalency of Fe^{3+}-oxygen bonds. If Fe^{3+} ions occupy 0.2 of the 6 Si sites, the implied ε-value for the 20100 cm^{-1} tetrahedral-Fe^{3+} band is ~ 10.

The ε-value of the 22700 cm^{-1} band in andradites (1-2) is considerably smaller than that observed (~ 500) for the corresponding band in synthetic $Gd_3Fe_5O_{12}$ garnet (Levenson & Sawatzky 1969). Absorption by Fe^{3+} ions is considerably more intense in Fe_2O_3 than in silicates. This indicates that $O^{2-} \to Fe^{3+}$ 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 $O^{2-} \to M^{3+}$ 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 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 ~ 24000 cm^{-1}. The 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

BERKES, J.S. (1968) : Energy level diagrams for transition metal ions in cubic crystal fields. *Materials Research Lab. Mono.* **2,** Pennsylvania State Univ.

BURNS, R.G. (1970) : *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press.

BURNS, R.G. & STRENS, R.G.J. (1967) : Structural interpretation of polarized absorption spectra of the Al-Fe-Mn-Cr epidotes. *Mineral. Mag.* **36,** 204.

BUERGER, M.J., BURNHAM, C.W. & PEACOR, D.R. (1962) : Assessment of the several structures proposed for tourmaline. *Acta Cryst.* **15,** 583.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962) : *Rock-Forming Minerals.* Longmans, London. Vol. **1.**

DINGLE, R. (1966) : The visible and near infrared spectrum of manganese (III) complexes. *Acta Chem. Scand.* **20,** 33.

FAYE, G.H. (1969) : The optical absorption spectrum of tetrahedrally-bonded Fe^{3+} in orthoclase. *Can. Mineral.* **10,** 112.

FAYE, G.H. & HOGARTH, D.D. (1969) : On the origin of reserve pleochroism of a phlogopite. *Can. Mineral.* **10,** 25.

FAYE, G.H., MANNING, P.G. & NICKEL, E.H. (1968) : The polarized optical absorption spectra of tourmaline, cordierite, chloritoid and vivianite. *Amer. Mineral.* **53,** 1174.

HARTMAN, P. (1969) : Can Ti^{4+} replace Si^{4+} in silicates. *Mineral. Mag.* **37,** 366.

KURKJIAN, C.R. & SIGETY, E.A. (1968) : Coordination of Fe^{3+} in glass. *Phys. Chem. Glasses.* **9,** 73.

LEVENSON, M. & SAWATZKY, E. (1969) : Optical absorption in gadolinium iron garnet. *J. Appl. Phys.* **40,** 2672.

MANNING, P.G. (1967) : The optical absorption spectra of some andradites and the identification of $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition in octahedrally-bonded Fe^{3+}. *Can. J. Earth Sci.* **4,** 1039.

MANNING, P.G. (1969a) : Optical absorption spectra of chromium-bearing tourmaline, black tourmaline and buergerite. *Can. Mineral.* **10,** 57.

MANNING, P.G. (1969b) : An optical absorption study of the origin of colour and pleochroism in pink and brown tourmalines. *Can. Mineral.* **9,** 678.

MANNING, P.G. (1970) : Racah parameters and their relationship to length and covalencies of Mn^{2+} and Fe^{3+} oxygen bonds in silicates. *Can. Mineral.* **10,** 677.

MANNING, P.G. & TOWNSEND, M.G. (1970) : Effect of next-nearest-neighbour interaction on oscillator strengths in garnets. *J. Phys. Clem.* **3,** L14.

MANNING, P.G. (1972) : Optical absorption spectra of Fe^{3+} in octahedral and tetrahedral sites in natural garnets. *Can. Mineral.* **11,** 826-839.

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