

AN OPTICAL ABSORPTION STUDY OF THE ORIGIN OF COLOUR AND PLEOCHROISM IN PINK AND BROWN TOURMALINES

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ABSTRACT

An optical absorption study of the origin of the colour and pleochroism of pink (elbaïtes) and brown (dravites) tourmalines is reported. Simple ligand-field theory is used in assigning absorption bands of polarised tourmaline spectra to specific transition-metal ions in specific environments. The pleochroic properties of the bands are correlated with some structural properties of the crystal.

It is suggested that the colour of pink and brown tourmalines is due to *d-d* electronic transitions in octahedrally-bonded Mn³⁺ and Ti ions, respectively. Pink tourmalines have an absorption band at 19,000 cm⁻¹ (520 mμ) and brown tourmalines a band at 22,000 cm⁻¹ (450 mμ). The bands in both systems have maximum intensity when the electric vector of incident light is vibrating in the 001 plane and the probable causes of the pleochroism are discussed. It is also concluded that the transition metal ions are located mainly in the trigonal brucite units.

INTRODUCTION

Although colour has always been regarded as a fundamental property of a (coloured) mineral, it is only very recently that concerted attempts have been made to elucidate its origin in specific minerals (e.g., Burns & Strens, 1967). In particular, the absorption of light (including infrared and ultraviolet radiation) of a given wavelength can often be assigned to electronic transitions between well-defined electronic energy-levels in transition-metal ions. These transitions characterise the cation, its valence state and the nature of its environment in the crystal.

In the present work, dealing with pink and brown tourmalines, the assignment of absorption bands is based on simple ligand-field theory. Suitable introductions to the theory of *d*-orbital-splittings in a ligand (anion) field have been written by Cotton & Wilkinson (1967) and Figgis (1967). The reader is also referred to papers by Burns & Strens (1967) and Schwarcz (1967).

The origin of the colour of pink tourmalines has long been the subject of debate among mineralogists. The many suggestions proposed have been reported by Slivko (1959), but no attempts have been made to explain the colour and pleochroism in terms of ligand field theory. What

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is known from chemical analyses of several pink tourmalines (Slivko, 1959; Bradley & Bradley, 1953) is that Mn is the responsible cation. Similarly, it has long been known that Fe is the principal colour-producing agent in green tourmalines (e.g., see Slivko, 1959 and Bradley & Bradley, 1953), even though green tourmalines often contain considerably more Mn than the pink tourmalines. The pink tourmalines must absorb light in the green region, while the green tourmalines transmit light in the green region. Because it is known from ligand-field theory that electronic transitions in Mn^{2+} are spin-forbidden and that transitions in Mn^{3+} are spin-allowed (Cotton & Wilkinson, 1967), it is possible that the different effects of manganese on the colour of tourmalines can be attributed to valency differences.

In this paper, therefore, a detailed study is made of the absorption spectra and pleochroism of pink tourmalines. This study also includes brown tourmalines (dravites) because the proposed mechanism for pleochroism, although involving Ti, is different. It should be noted that the dravite work is not of secondary importance: the emphasis of the above discussion on pink tourmalines is due simply to the fact that more work has been published on the origin of colour in the latter.

In a recent spectral study of green and blue tourmalines (Faye, Manning & Nickel, 1968), it was proposed that the colour and pleochroism was due in part to an $Fe^{2+} \rightarrow Fe^{3+}$ electron-hopping process involving iron ions in adjacent octahedral sites. The Fe^{2+} - Fe^{3+} electron-hopping reaction is characterised by a pleochroic absorption band at $\sim 14,000\text{ cm}^{-1}$ with maximum intensity when the electric vector vibrates in the 001 plane. This plane contains layers of cations sharing octahedral edges, a pre-requisite for t_{2g} - t_{2g} orbital overlap.

MATERIALS

Three pink tourmalines and two "water-melon" tourmalines*, from different localities, were examined. The spectra reported in this paper pertain to the pink area of a "water-melon" tourmaline from Mesa Grande, California. The spectra of all five crystals are very similar.

Two brown tourmalines (var. dravite) were examined, and the spectra presented here are those of a specimen from Gouverneur, New York. The spectra are quite representative of the two brown dravites.

The tourmalines were kindly donated by Messrs. H. R. Steacy and L. Moyd, curators of the research and display sections respectively, of the National Mineral Collection.

*A water-melon tourmaline is one that has a pink core and a green rim.

EXPERIMENTAL DETAILS

Crystals of dimensions of at least 2 mm \times 2 mm (length \times breadth) were mounted in one window of a two-windowed variable-aperture crystal holder. The holder fitted the cell compartment of a Beckman DK-2A double-beam spectrophotometer. An oriented polaroid film covering both sample and reference beams, was used to obtain polarised light. Some spectra were also run on a Cary 14 spectrophotometer. All spectra were run at room temperature.

Sections were cut parallel and perpendicular to the c crystallographic axis since, for uniaxial crystals, only $E \perp c$ and $E \parallel c$ need be considered. Here, E represents the direction of polarisation of the electric vector of the light incident on the plane of the section. Sections cut parallel to the c -axis (hereafter called parallel sections) gave good optical interference figures characteristic of uniaxial flash figures, and those cut perpendicular to c , (hereafter called 001 sections) gave a centred uniaxial cross.

The extinction coefficient is defined as:

$$\frac{\text{absorbance}}{\text{sample thickness (cm)} \times \text{cation concentration (moles/litre)}}$$

Crystal thicknesses were measured with a micrometer.

STRUCTURE OF TOURMALINE

The structure of dravite, ideally $\text{NaMg}_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH})_4$, has been determined by Donnay & Buerger (1950). Each magnesium ion is surrounded by four oxygen and two (OH) ions at distances varying from 2.08 to 2.24 Å, and forming a fairly regular octahedron. The octahedra are combined in groups of three, each one sharing two of its octahedral edges with its neighbours in the 001 plane. The arrangement is similar to that in the brucite structure, and these groups can be regarded as "trigonal brucite units." Each of the Mg/Fe-O/OH octahedra also shares another two octahedral edges with distorted Al-centred octahedra, which have Al-O/OH bond distances ranging from 1.76 to 2.25 Å.

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. This results in spiral chains of Al-octahedra parallel to the c -axis. The relationships between the Mg and Al ions are illustrated in Fig. 1.

According to the numerous chemical analyses listed in Deer, Howie & Zussman (1962), it would seem that transition-metal ions preferentially

occupy the Mg sites, and Faye, Manning & Nickel (1968) have interpreted the absorption spectra of blue and green tourmalines in terms of Fe^{2+} and Fe^{3+} ions occupying the trigonal units preferentially.

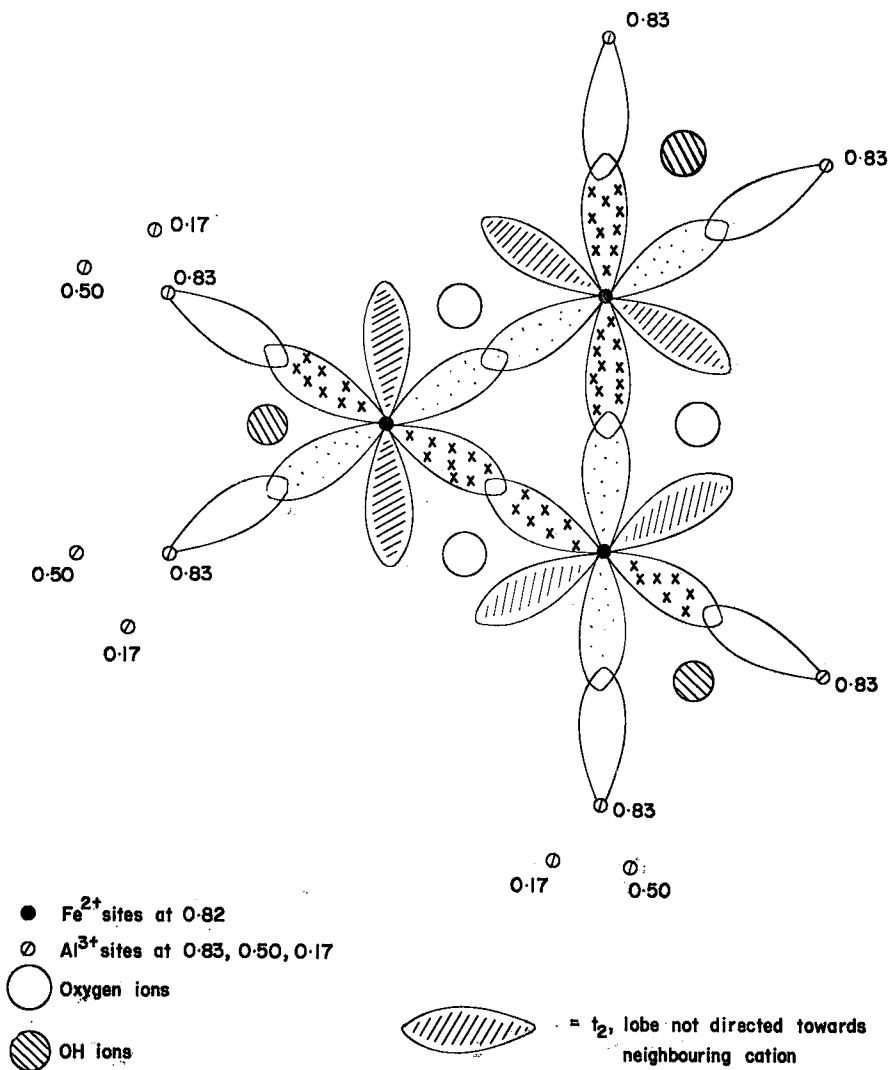


FIG. 1. Representation of tourmaline structure, showing Mg and Li/Al sites in the trigonal brucite fragments and the Al sites in the spiral chains. Diagram is a projection on 001 plane, the oxygen and OH ions are above the plane. Also shown is t_{2g} - t_{2g} orbital overlap between neighbouring cations.

The structure of a pink tourmaline, rubellite, $(\text{Na,Ca})(\text{Li,Al})_3\text{Al}_6(\text{OH})_4(\text{BO}_3)_3\text{Si}_6\text{O}_{18}$, has been determined by Ito & Sadanaga (1951). The Li/Al-O/OH bond lengths range from 1.95–2.04 Å, while the Al-O/OH bond lengths range from 1.76–2.25 Å. The Li/Al ions are octahedrally-coordinated in the trigonal units. Ito & Sadanga (1951) point out that (Li,Al) occupy the same structural positions as those occupied by Mg in dravite, and that they are similar in coordination form and character, being situated in the middle of a fairly regular octahedron of 4 oxygens and 2 OHs.

INTERPRETATION OF SPECTRA

Absorption spectra of dravites

Figure 2 presents the $E \perp c$, $E // c$ and unpolarised-light spectra of parallel sections of the Gouverneur dravite. Certain absorptions in the spectra were also observed in the spectra of green and blue tourmalines studied earlier (Faye, Manning & Nickel, 1968), namely, the absorptions at $9,500 \text{ cm}^{-1}$ and $14,500 \text{ cm}^{-1}$. The former band marks the ${}^5T_2 \rightarrow {}^5E$ transition in octahedrally-bonded Fe^{2+} . The polarised $14,500 \text{ cm}^{-1}$ band

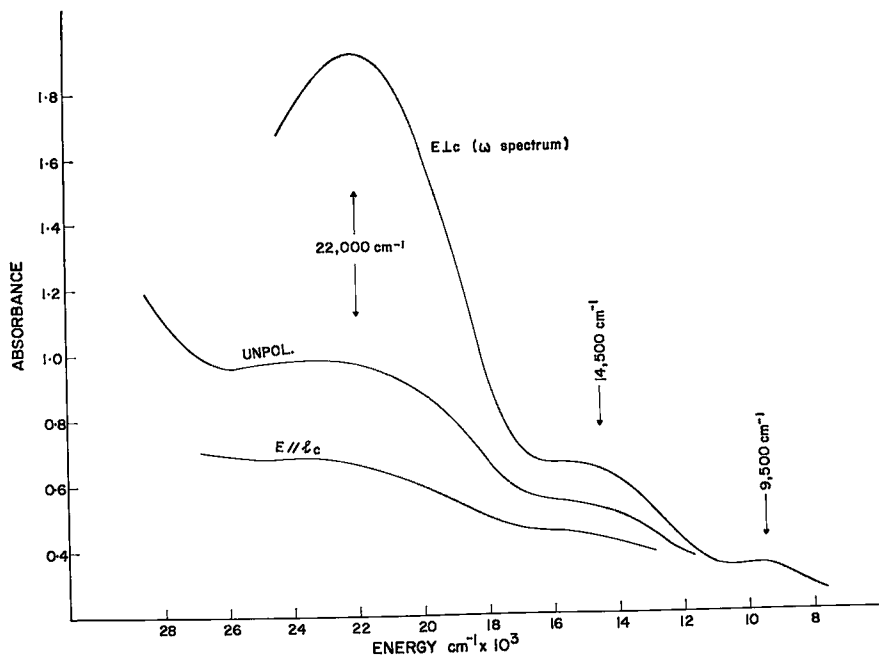


FIG. 2. Optical absorption spectra of a parallel section of dravite. Sample thickness = 0.038 cm. UNPOL designates unpolarised-light spectrum.

probably corresponds to the polarised $13,900\text{ cm}^{-1}$ band that is a major colour-producing band in green and blue tourmalines. This absorption was assigned to an $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ electron-hopping process (Faye, Manning & Nickel, 1968). The dravite contains 1.01% Fe (Table 1), from which the extinction coefficient of the $9,500\text{ cm}^{-1}$ band is ~ 3 litres/mole-cm, and is consistent with $\epsilon \sim 4$, in the previous work.

TABLE 1. CHEMICAL ANALYSES OF DRAVITES AND ELBAITES

	Dravites		Elbaites		
	No. 1*	No. 2	No. 1*	No. 2	No. 3
% Fe	1.01	4.92	0.85	0.21	0.40
% Mn	0.05		0.16	0.19	0.28
% Ti	1.15	0.96	0.06	0.007	

*Spectra in Figs. 2-4 refer to these samples.

In the dravites, the $14,500\text{ cm}^{-1}$ band has little influence on the colour of the crystal (Fig. 2), since the spectrum is dominated by the strongly pleochroic absorption band at $22,000\text{ cm}^{-1}$, which has its maximum intensity when $E \perp c$, i.e., when the electric vector is vibrating in the plane of the trigonal Mg units. The energy of the band maximum changes very little in the $E \perp c$, $E // c$ and unpolarised-light spectra.

The $22,000\text{ cm}^{-1}$ band cannot be associated with the presence of Fe because the band is not observed in blue tourmalines that contain considerably more Fe (Faye, Manning & Nickel, 1968). Where Mn is the predominant cation absorbing in the visible region, the tourmalines are pink, indicating absorption of green and blue light (e.g., Bradley & Bradley, 1953); hence the $22,000\text{ cm}^{-1}$ band is unlikely to be due to Mn.

Titanium is often present in silicates, and the dravite whose spectrum is given in Fig. 2 contains 1.1% Ti. Chemical analyses for total Fe, Mn and Ti for some of the tourmalines examined are given in Table 1. The $\text{Ti}^{3+}:\text{Ti}^{4+}$ ratio for the dravite is not known, but based on the total Ti content, the extinction coefficient of the band in unpolarised light (Fig. 2) is 12 litres/mole-cm. This extinction coefficient is of reasonable magnitude for an intracationic $d-d$ band of Ti^{3+} and is not inconsistent with Ti^{3+} being in a centro-symmetric site (Burns & Strens, 1967). The extinction coefficient of the $22,000\text{ cm}^{-1}$ band in the second dravite is 18 litres/mole-cm.

Although the $\text{Ti}^{3+}:\text{Ti}^{4+}$ ratio is not known, the $22,000\text{ cm}^{-1}$ band would seem to be at too high an energy for the ${}^2T_2 \rightarrow {}^2E(D)$ transition in octahedrally-bonded Ti^{3+} in silicates. This transition is observed at $19,000\text{ cm}^{-1}$ in andradite (Manning, 1967), $17,200\text{ cm}^{-1}$ in chloritoid

(Faye, Manning & Nickel, 1968) and $17,500\text{ cm}^{-1}$ in star sapphire (White & White, 1967). The andradite and chloritoid contained 5% Ti, mostly as Ti^{3+} . The ${}^2T_2 \rightarrow {}^2E(D)$ transition is observed at $20,300\text{ cm}^{-1}$ in $\text{Ti}(\text{OH}_2)_6^{3+}$ (Hartmann & Schlafer, 1951).

Although the $\text{Ti}^{3+}:\text{Ti}^{4+}$ ratio is not known, the $22,000\text{ cm}^{-1}$ band, nevertheless is at a very reasonable energy for the ${}^2T \rightarrow {}^2E(D)$ transition in Ti^{3+} . The corresponding transition is observed at $20,300\text{ cm}^{-1}$ in $\text{Ti}(\text{OH}_2)_6^{3+}$ (Hartmann & Schlafer, 1951). Significantly, the extinction coefficient of the $22,000\text{ cm}^{-1}$ band in the second dravite is 18 litres/mole-cm.

The intensity of the $22,000\text{ cm}^{-1}$ band is greatest in the $E \perp c$ spectrum (Fig. 2). This could be explained as follows: six orbital lobes, representing two lobes of each of the three t_{2g} orbitals of a cation located in the trigonal units, lie in the trigonal plane, and four of these lobes, two from each of two t_{2g} orbitals, are directed towards neighbouring cations of the trigonal units and neighbouring cations of the Al^{3+} ions in the spiral chains. Because of the net positive charge on these cation neighbours, the $3d$ electron of Ti^{3+} can be expected preferentially to occupy these lobes. Hence, interaction with radiation is greatest in this cation plane, represented by the $E \perp c$ spectra. Since very little interaction would be expected when $E \parallel c$, this would seem to be a reasonable explanation for the marked pleochroism of brown dravites.

The $22,000\text{ cm}^{-1}$ band is also weakly observed in $E \parallel c$ spectra of parallel sections of dravite (Fig. 2). It is possible that a small fraction of the Ti^{3+} is located in the spiral chains. These chains run parallel to the c -axis and metal-metal t_{2g} d -orbital overlap also occurs here. The projection of this d -orbital overlap on a plane parallel to the c -axis is large, and the $t_{2g} \rightarrow e_g$ transition will have appreciable intensity in $E \parallel c$ spectra. The much greater intensity of the $22,000\text{ cm}^{-1}$ band in $E \perp c$ spectra (Fig. 2) indicates that most of the Ti^{3+} is in the trigonal units.

However, there are serious objections to this theory. The absorption band marking the ${}^2T_2 \rightarrow {}^2E(D)$ transition in Ti^{3+} in chloritoid is non-pleochroic (Faye, Manning & Nickel, 1968). Whether the Ti^{3+} is in the brucite or corundum layers of chloritoid, t_{2g} - t_{2g} orbital overlap occurs in the 001 plane, and accordingly it must be concluded that the Ti^{3+} d -electron is not localised in lobes directed towards neighbouring cations. Also, as already mentioned, the $22,000\text{ cm}^{-1}$ would seem to be at too high an energy compared with the energy of the ${}^2T_2 \rightarrow {}^2E(D)$ transition in Ti^{3+} observed in other silicates (andradite, chloritoid and star sapphire).

The pleochroism of the $22,000\text{ cm}^{-1}$ band is related to the crystallographic axes of tourmaline, the band having maximum intensity in $E \perp c$ spectra and minimum in $E \parallel c$. In this way, the pleochroism of the

22,000 cm^{-1} band in the brown tourmalines is similar to the pleochroic scheme exhibited by the $\sim 14,000 \text{ cm}^{-1}$ band in green and blue tourmalines that marked $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ electron-hopping in the 001 plane. It seems logical to suggest that the 22,000 cm^{-1} band in brown tourmalines marks a $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ electron transition, by way of overlapping t_{2g} orbitals in the 001 plane. $\text{Ti}^{3+} \rightarrow \text{Ti}^{3+}$ electron-hopping seems unlikely because a band corresponding to such a transition is not observed in chloritoid (Faye, Manning & Nickel, 1968).

Jorgensen (1957) has assigned an absorption band at 21,000 cm^{-1} in the spectrum of a dimer, $\text{Ti(IV) \cdot Ti(III)Cl}_x$, formed in strong HCl solution, to $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ electron-transfer by way of an intermediate Cl^- ion. Manning (1969) has also suggested that the colours of astrophyllite and brown clintonite are due to $\text{Ti}^{3+}\text{-Ti}^{4+}$ interaction, the principal colour-forming bands being at 23,300 cm^{-1} and 22,000 cm^{-1} respectively. Astrophyllite also exhibits a weak band at 17,000 cm^{-1} that is assigned to the ${}^2T_2 \rightarrow {}^2E(D)$ transition in Ti^{3+} . The pleochroic 23,000 cm^{-1} band in astrophyllite has maximum intensity in $E \perp (001)$ spectra, coinciding with the directions of Ti-O-Ti units.

Absorption spectra of pink tourmalines

The absorption spectra of parallel and basal sections of a pink region of a "water-melon" tourmaline are shown in Figs. 3 and 4, respectively. The pleochroism of parallel sections is due mainly to the pleochroic properties of the band at 19,200 cm^{-1} . The review by Slivko (1959) suggests the absorbing cation is Mn.

The spectra in Figs. 3 and 4 are markedly different from the absorption spectra of octahedrally-bonded Mn^{2+} in $\text{Mn(OH}_2)_6^{2+}$ (Heidt, Koster & Johnson, 1958) and in silicates (Manning, 1968). In particular, the impressively sharp band at $\sim 25,000 \text{ cm}^{-1}$ that marks the field-independent transition (${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$) in Mn^{2+} is absent. This suggests that the manganese in the pink tourmaline is probably not divalent.

For Mn^{3+} in weak oxygen fields, e.g., $\text{Mn(oxalate)}_3^{3-}$, the only spin-allowed band is observed at 20,000 cm^{-1} (Furlani & Ciana, 1958). This is in good agreement with the energy of the 19,200 cm^{-1} band in pink tourmaline (Figs. 3 and 4). The 19,200 cm^{-1} band is also by far the most intense $d-d$ band in the spectrum.

Based on the total Mn concentration of 0.16% (Table 1), the extinction coefficient of the 19,200 cm^{-1} band in the unpolarised-light spectrum of Fig. 3 is 15 litres/mole-cm, a reasonable value for a spin-allowed intracationic $d-d$ band in general. Because of the weakness of field-independent Mn^{2+} bands at $\sim 25,000 \text{ cm}^{-1}$, it would seem that most of the Mn would be present as Mn^{3+} . Therefore, the energy and intensity of the 19,200

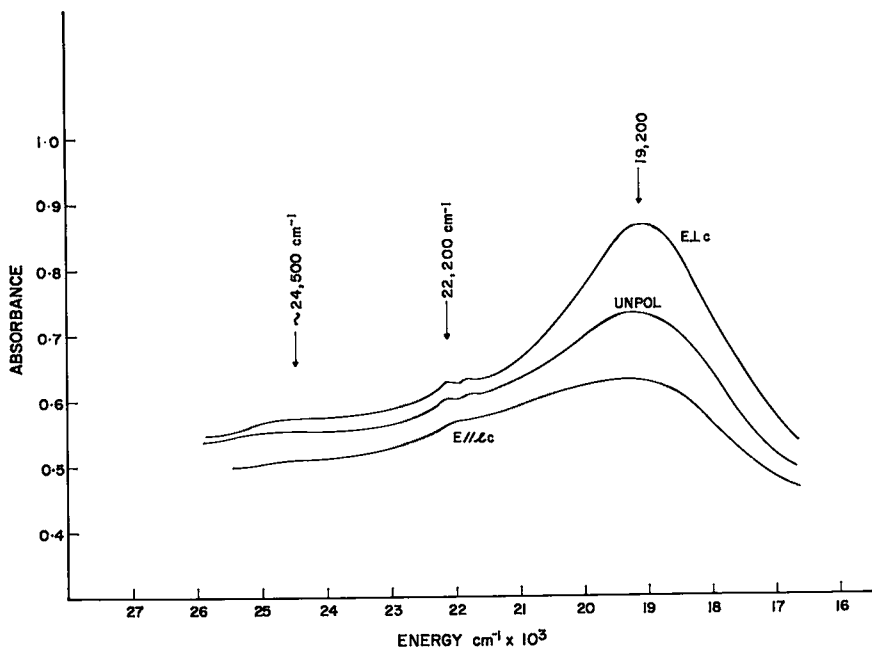


FIG. 3. Absorption spectra of parallel sections of pink tourmaline. Sample thickness = 0.165 cm.

cm^{-1} band in pink tourmaline are not inconsistent with its being assigned to the ${}^5E \rightarrow {}^5T_2(D)$ transition in Mn^{3+} .

The two very weak, but very sharp peaks at 21,900 cm^{-1} and 22,200 cm^{-1} are observed in the spectra (Figs. 3 and 4) of all five pink tourmalines. Their intensities change, from crystal to crystal, in unison with that of the 19,200 cm^{-1} band, suggesting that they are all possibly due to the same cation. A Tanabe-Sugano (1954) energy-level diagram for Mn^{3+} in weak cubic fields is presented in Fig. 5. Assuming that the reduction in free-ion terms is small, and assigning the 19,200 cm^{-1} band to the transition ${}^5E \rightarrow {}^5T_2(D)$ in octahedrally-bonded Mn^{3+} , then it is evident that the two sharp peaks are at approximately the right energy for the doubly-spin-forbidden transitions ${}^5E \rightarrow {}^7T_2(I)$ and ${}^5E \rightarrow {}^7E(I)$ (Fig. 5). Alternatively, the two sharp peaks could mark electronic transitions to the lowest field-independent states, ${}^6A_1 \rightarrow {}^4A_1$ and ${}^4E(G)$, in octahedrally-bonded Fe^{3+} . It is evident from Fig. 5, that the 7E and 7T_2 states are steeply sloping at the inferred Δ value for Mn^{3+} (dotted line in Fig. 5), hence it would seem much more reasonable assigning the two sharp peaks to Fe^{3+} . Sharp bands at 22,400 cm^{-1} and 22,700 cm^{-1} attributable to octahedrally-bonded Fe^{3+} have been observed in the spectra of andradites (Manning, 1967).

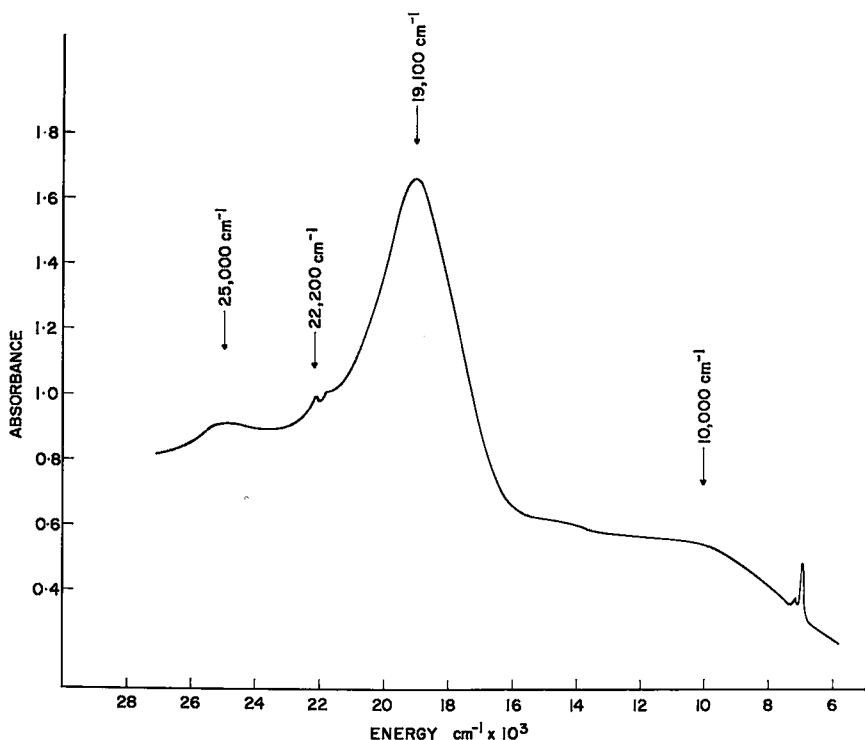


FIG. 4. Absorption spectrum in unpolarised light of basal section of pink tourmaline. Thickness of sample = 0.35 cm.

The 19,200 cm^{-1} band in spectra of the pink tourmalines could be due to a $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ electron-hopping process. Because the pleochroism of the band is related to the crystallographic axes of tourmaline in the same way as is the 22,000 cm^{-1} band in brown tourmalines, the electron-transfer process is either $t_{2g}(\text{Mn}^{2+}) \rightarrow t_{2g}(\text{Mn}^{3+})$ or $t_{2g}(\text{Mn}^{2+}) \rightarrow e_g(\text{Mn}^{3+})$. The latter process will occur at a much lower energy than the former because the electronic ground state of $\text{Mn}^{2+}(d^5)$ is $t_{2g}^3e_g^2$. The 19,200 cm^{-1} band in pink tourmalines could, therefore, mark an electron transition from the t_{2g} orbital of Mn^{2+} to the unoccupied antibonding e_g orbital of Mn^{3+} . However, because of the orthogonal relationship between t_{2g} and e_g orbitals, net orbital overlap in such a system is zero and transitions may occur with less probability. Nevertheless, the fact that the 19,200 cm^{-1} band has maximum intensity in $E \perp c$ spectra seems to suggest that the band is a metal \rightarrow metal interaction band.

The presence of the two Fe^{3+} peaks on the high-energy limb of the 19,200 cm^{-1} band (Figs. 3 and 4) is of interest because Fe^{3+} intracation $d-d$ bands are not observed in the spectra of green and blue tourmalines

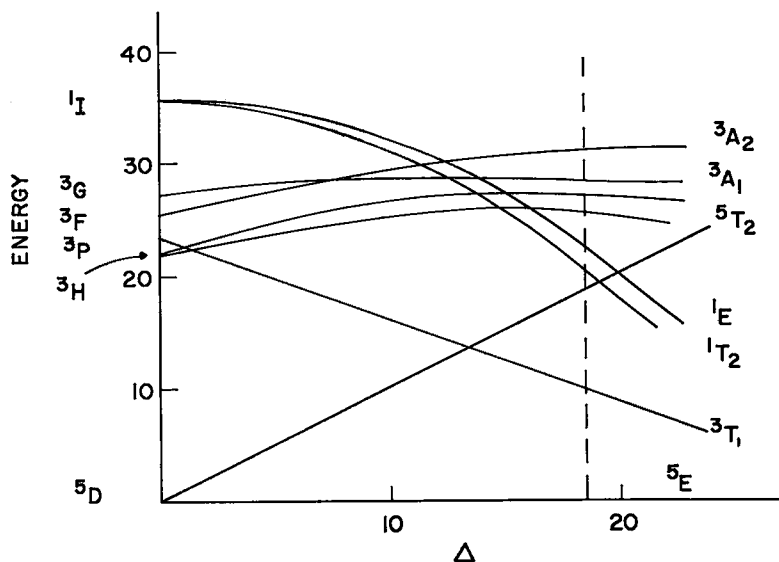


FIG. 5. Energy-level diagram for d^4 cation in an octahedral field. Dotted line is inferred Δ value in order to fit observed transitions. Energies in $\text{cm}^{-1} \times 10^3$.

(Faye, Manning & Nickel, 1968), even though the latter minerals contained much more Fe. It is likely that the Fe^{3+} intracation $d-d$ bands in green and blue tourmalines are "swamped" by the spin-forbidden bands of Fe^{2+} that appear in the high-energy and of the visible region. Assuming an extinction coefficient of 1 for the ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$ transition in Fe^{3+} , calculations indicate that 50% or more of the Fe in the pink tourmalines examined here is present as Fe^{3+} . Chemical analyses of some pink tourmalines listed in Deer, Howie & Zussman (1962) and Bradley & Bradley (1953) suggest that the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio in pink tourmalines is often considerably higher than in green and blue tourmalines. Therefore, because the intensities of the two sharp Fe^{3+} peaks and the 19,200 cm^{-1} band seem to be related, and, further, because the colour of pink tourmalines is due in some way to the presence of Mn, then a possible cause of the 19,200 cm^{-1} band is $\text{Mn}^{2+} \rightarrow \text{Fe}^{3+} (t_{2g} \rightarrow t_{2g})$ electron-transfer. We would favour this proposal rather than a $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ interaction.

The broad, pleochroic band at $\sim 24,500 \text{ cm}^{-1}$ appears in the spectra (Figs. 3 and 4) of all pink tourmalines, and its intensity is also related to the crystallographic axes of tourmaline. The intensity of this band is approximately proportional to the intensity of the 19,200 cm^{-1} band. The $\sim 24,500 \text{ cm}^{-1}$ band has maximum intensity in $E \perp c$ spectra, and it could also mark metal \rightarrow metal electron-transfer, possibly $t_{2g}(\text{Mn}^{2+}) \rightarrow e_g(\text{Fe}^{3+})$. However, the energy difference between the transitions

$t_{2g}(\text{Mn}^{2+}) \rightarrow t_{2g}(\text{Fe}^{3+})$ and $t_{2g}(\text{Mn}^{2+}) \rightarrow e_g(\text{Fe}^{3+})$ should equal 10 Dq for Fe^{2+} in weak ligand fields, i.e. $\sim 9,000 \text{ cm}^{-1}$. The observed difference 24,500-19,200 cm^{-1} is, however, considerably smaller than this. Nevertheless, the 19,200 cm^{-1} and the weaker $\sim 24,500 \text{ cm}^{-1}$ bands could be $\text{Mn}^{2+} \rightarrow$ metal electron-transfer bands.

In the $E//c$ spectrum of Fig. 3, the main envelope is considerably broadened, due to a poorly-defined shoulder at $\sim 21,000 \text{ cm}^{-1}$ on the high-energy side of the 19,200 cm^{-1} band. This shoulder is only weakly evident in the $E \perp c$ spectrum, possibly because it is "swamped" by the 19,200 cm^{-1} band. The 21,000 cm^{-1} band could be due to $\text{Mn}^{2+} \rightarrow$ metal³⁺ interaction in the spiral Al^{3+} chains.

It would seem that $\text{Mn}^{2+} \rightarrow$ metal³⁺ electronic transitions are not entirely satisfactory in explaining the colour of pink tourmaline. It is more likely that the 19,200 cm^{-1} band (Figs. 3 and 4) in pink tourmaline marks the ${}^5E \rightarrow {}^5T_2(D)$ transition in Mn^{3+} and that the pleochroism of the band may be due to greater vibronic coupling in $E \perp c$ spectra. The 21,000 cm^{-1} band could then be assigned to a Jahn-Teller (1937) mechanism arising from the $t_{2g}{}^3e_g{}^1$ configuration of Mn^{3+} . The broad band at 24,500 cm^{-1} could mark spin-forbidden transitions to a number of triplets levels in Mn^{3+} (Fig. 5). The change in intensity of the Fe^{3+} bands (at $\sim 22,000 \text{ cm}^{-1}$) in unison with the 19,200 cm^{-1} Mn^{3+} band may be due to a geochemical correlation of Mn with Fe.

The difference in colour between blue and green tourmalines is due (Faye, Manning & Nickel, 1968) largely to a pleochroic absorption band present in green tourmalines at $\sim 22,000 \text{ cm}^{-1}$. On the basis of the present work this band could be due to Ti^{3+} - Ti^{4+} interaction in the trigonal units. Based on total Ti concentrations, the extinction coefficient of the 22,000 cm^{-1} band in some green tourmalines is ~ 25 , a value somewhat greater than for Ti in dravites, but still reasonable. It has been suggested, however, that a similar broad band at $\sim 24,000 \text{ cm}^{-1}$ in the spectra of certain sheet silicates might be due to the electronic interaction of Fe^{2+} and Ti^{3+} or Ti^{4+} (Faye, 1968).

CONCLUSION

The colour of pink tourmalines has been attributed to $d-d$ electronic transitions in octahedrally-bonded Mn^{2+} . The colour and pleochroism of brown tourmalines would seem to be due to $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ electron-transfer.

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