

High-temperature, high-pressure optical spectroscopic study of ferric-iron-bearing tourmaline

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ABSTRACT

The optical spectra of dravite (tourmaline) with an unusually high ratio of Fe³⁺ to Fe²⁺ and a synthetic elbaite with high Fe³⁺ content were studied at high temperature (297 to 600 K) and high pressure (to 10.51 GPa) conditions. Individual absorption bands derived from paired Fe atoms were identified in the spectra and their temperature and pressure dependence was studied. The most pronounced effects are the intensification of the two Fe²⁺-related bands (~9090 cm⁻¹ and ~14300 cm⁻¹) at pressure, their shift to higher energy at pressure, and their pronounced intensity decrease with increasing temperature. Such behavior is assumed to be caused by an electronic exchange interaction in an Fe²⁺-Fe³⁺ pair at adjacent Y sites in the structure.

Temperature and pressure dependencies of the bands attributed to Fe³⁺-Fe³⁺ exchange-coupled pairs are noticeably different from those of Fe²⁺-Fe³⁺ pairs. This shows that the two types of pairs have different exchange interactions, and points to the need for further experimental and theoretical investigation.

The intensity of the intense E_{Lc}-polarized band at ~20580 cm⁻¹ originating from the ⁶A_{1g} → (⁴A_{1g}, ⁴E_g) transition of the Fe³⁺(Y)-Fe³⁺(Y) pair, depends moderately on temperature and pressure. The intensity of a weak shoulder at ~18350 cm⁻¹ (E_{Lc}), also attributed to an Fe³⁺(Y)-Fe³⁺(Y) pair, decreases and nearly disappears between 5.44 and 9.55 GPa. The intensity of the E_{llc}-polarized band at ~18500 cm⁻¹, attributed to an Fe³⁺(Z)-Fe³⁺(Z) pair, displays a strong inverse temperature dependence, whereas the energy of the band remains nearly constant.

INTRODUCTION

The spectroscopy of the tourmaline group is not fully understood, in part because of complicating interactions between and among ions in the many cation sites. Many of the complications derive from iron and its interactions, which strongly influence the color, pleochroism, and spectroscopic properties by an exchange-coupling interaction between ferrous and ferric ions. This interaction causes intensification of the spin-allowed crystal-field ³T_{2g} → ⁵E_g bands of Fe²⁺ at Y sites adjacent to Y sites occupied by Fe³⁺ (Smith and Strens 1976; Smith 1978; Mattson and Rossman 1987). Because the Fe²⁺-Fe³⁺ interaction dominates within the Y site trimers and is much weaker in the Z site helixes along the c axis, both natural (Smith 1978; Mattson and Rossman 1987) and synthetic (Fe²⁺, Fe³⁺)-bearing tourmalines (Taran et al. 1993) display strong dichroism E_{Lc} >> E_{llc}.

Optical absorption bands attributed to the electronic dd transitions of ferric ions have been assigned in natural (Mattson and Rossman 1984) and in synthetic tourmalines (Taran et al. 1993). These bands differ in their intensity, energy, and width from the corresponding bands in spectra of Fe³⁺-bearing minerals and compounds where ferric ions occupy "isolated" structural sites. For this reason, Mattson and Rossman (1984) attributed them to electronic transitions of Fe³⁺-Fe³⁺ exchanged-coupled pairs in trimers and helixes of the tourmaline structure.

Absorption bands of Fe²⁺ enhanced by exchange interaction in Fe²⁺-Fe³⁺ pairs display unusual temperature and pressure

dependencies that are different from those of ordinary spin-allowed dd bands of "isolated" Fe²⁺ (e.g., Smith and Strens 1976; Smith 1978; Mattson and Rossman 1987; Taran et al. 1996). By analogy, one might expect a similar situation for bands caused by electronic transitions of Fe³⁺-Fe³⁺ exchange-coupled pairs. From this point of view, it is interesting to investigate the temperature and pressure behavior of optical-absorption spectra of Fe³⁺-rich tourmaline.

In this work, the results of a high-temperature and high-pressure optical spectroscopic study of an unusual red ferrian dravite from Kenya are presented. Because about 90% of the iron in this dravite is Fe³⁺, the highest percentage of ferric iron so far found in a natural tourmaline, its characterization is of fundamental importance. Additional detailed characterization of this tourmaline, including its chemical composition, optical and Mössbauer spectra, and crystal structure have been presented by Bank (1974), Dunn et al. (1975), Mattson and Rossman (1984) and Hawthorne et al. (1993).

Previously, a synthetic, hydrothermally grown, Fe³⁺-doped tourmaline was measured in the 380–1000 nm range (Taran et al. 1993, Sp. 5) that shows a number of similarities to the natural tourmaline in question. For comparison, it was re-investigated here in the broader spectral range 350–2500 nm. By microprobe analysis, this sample contains 4.52 wt% FeO or 0.61 Fe³⁺ atoms per formula unit (apfu) (Taran et al. 1993).

EXPERIMENTAL DETAILS

Samples for investigation were prepared as oriented, transparent, self-supporting plates, polished on both sides. The

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planes of the samples contain the crystallographic *c* axis for measuring polarized spectra at ambient pressure. The samples of natural tourmaline were cut from a 1 cm, homogeneously colored dark-red crystal of dravite from Osarara, Narok District, Kenya (U.S. National Museum of Natural History number 126030). The initial orientation of the samples was performed using the well-developed prismatic habit of the crystal and confirmed by conoscopic interference figures obtained with a polarizing microscope. Two samples, 0.158 mm and 1.02 mm thick, were prepared for spectroscopic measurement in the ranges 350–500 and 450–2500 nm, respectively.

The synthetic tourmaline sample was prepared as a 0.22 mm thick slice. The sample was oriented in accordance with the initial orientation of the seed plate covered by an overgrowth layer of synthetic tourmaline and checked using conoscopic interference figures obtained with a polarizing microscope. In the slice, the color of the newly grown material is yellow.

Polarized electronic spectra were scanned in the 340–2500 nm range with a single-beam microspectrophotometer based on a SpectraPro-275 triple-grating monochromator connected to a highly modernized MIN-8 polarizing mineralogical microscope and controlled by an IBM 486 PC. The diameter of the measuring spot did not exceed 400 μm . A miniature electric furnace with an electronic control device that provides temperature stability of ± 0.5 K was attached to the spectrophotometer to allow spectra acquisition at temperatures from 300 to 600 K.

The high-pressure spectra can only be scanned on thin samples in unpolarized light (Langer 1990). The sample for high-pressure measurement was prepared as a 0.05 mm thick slice oriented perpendicular to the *c* axis. High-pressure spectra were scanned in the range 340–1400 nm at 10^{-4} , 2.23, 5.44, 9.55, and 10.51 GPa.

The high-pressure diamond-anvil-cell technique was used as described elsewhere (Fursenko et al. 1983; Langer 1990). The gasket was machined from 300 μm thick hardened steel with a 300 μm diameter bore. Methanol/ethanol (4:1) served as a pressure medium. The ruby-fluorescence method was used for pressure calibration (Mao et al. 1979). The fluorescence was excited by a 200 W Hg lamp with a blue filter and was scanned with a Raman spectrometer. To calibrate the ruby luminescence, the Ne sharp-line emission (692.95 and 696.28 nm) was recorded on the same plot as the ruby R-line fluorescence.

Spectra were originally obtained and plotted as absorbance vs. wavelength. To evaluate energy, peak intensity, and half-widths of the bands, Peakfit 4.0 (Jandel Scientific) software was used to fit the spectra with Gaussian curves after they were converted to a linear wavenumber scale. Band shapes and the background in the range of the absorption edge were assumed to be Gaussian. It should be noted that because of an intense high-energy absorption edge in *E* \perp *c*-polarization, the results of the curve fitting in the high-energy range significantly depend on the choice of Gaussian function simulating the edge.

RESULTS

Tourmaline

The room-temperature (297 K) spectrum in the range 350–2500 nm is shown in Figure 1. In the range 300–1700 nm, the spectrum is identical to that published by Mattson and

Rossmann (1984). Vibrations of the hydroxyl groups undoubtedly cause a series of weak absorption lines in the 2200–2500 nm range. The weak, sharp bands between 1350 and 1500 nm (*E* \parallel *c*) are also generated by vibrational overtones of OH molecules.

Mattson and Rossmann (1984) attributed four bands, *a* to *d*, in *E* \perp *c*-polarization and one band *e* in *E* \parallel *c* to electronic transitions of iron ions. Broad bands *a* and *b* at ~ 9090 cm^{-1} (1100 nm) and $\sim 14\,300$ cm^{-1} (700 nm) are assigned to electronic transitions of Fe^{2+} , indicating 0.30 wt% FeO in the sample. The intense band *d* at 20580 cm^{-1} (486 nm) and a distinct shoulder *c* at ~ 18350 cm^{-1} (545 nm) are attributed to exchange-coupled Fe^{3+} - Fe^{3+} pairs in Y site trimers, and band *e* at $18\,500$ cm^{-1} (540 nm) in *E* \parallel *c*-polarization is interpreted as an electronic transition of Fe^{3+} - Fe^{3+} pairs in helices (Z site). The structural refinement of Hawthorne et al. (1993) confirmed that both oxidation states of iron reside in the Y site, and did not identify any iron in the Z site.

At elevated temperatures the high-energy absorption edge rises in intensity, shifts to lower energies, and thus strongly overlaps bands *a* to *e*. Judging from visual observation, the peak heights of all bands noticeably decrease so that band *b* and shoulder *c* almost are not discerned at 600 K (Fig. 2).

The results of curve fitting of the 297 and 600 K *E* \perp *c*-polarized spectra are shown in Figure 2. The characteristics of the resulting Gaussian components are compiled in Table 1. Besides bands *a* to *d*, visually seen in the *E* \perp *c* spectrum measured at room temperature, one additional weak band with a maximum around $21\,900$ cm^{-1} , labeled as *f*, is necessary to fit the spectra in the high-energy range (Fig. 2). Whether this band really exists or is an artifact of the curve fitting process is difficult to determine. Mattson and Rossmann (1984) observed a poorly defined band in this spectral range at ~ 440 nm ($\sim 22\,700$ cm^{-1}). We are inclined to believe that in this spectral range there is a relatively weak absorption band(s) the precise parameters of which are difficult to determine by fitting because of an intense absorption background of uncertain form. As a result, in spectra measured at different temperatures, the parameters of the *f* band are poorly determined, significantly varying in intensity, energy, and width (Table 1). One possibility is that the *f* band is a “cold” band (Fujiwara et al. 1972) caused by two-exciton transitions of exchange-coupled Fe^{3+} - Fe^{3+} pairs that should gain intensity at

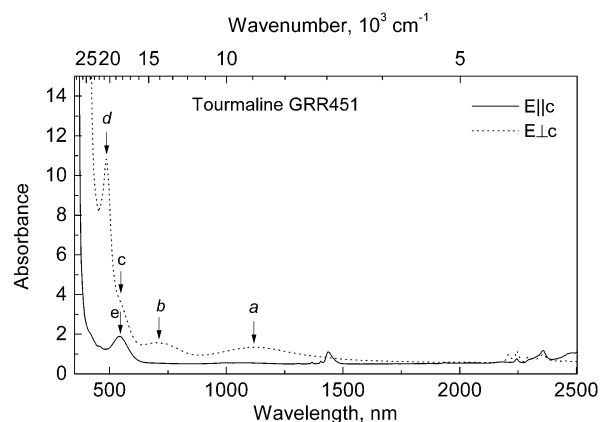


FIGURE 1. Polarized spectra of red ferrian dravite at ambient temperature and pressure. The sample thickness is 1.02 mm.

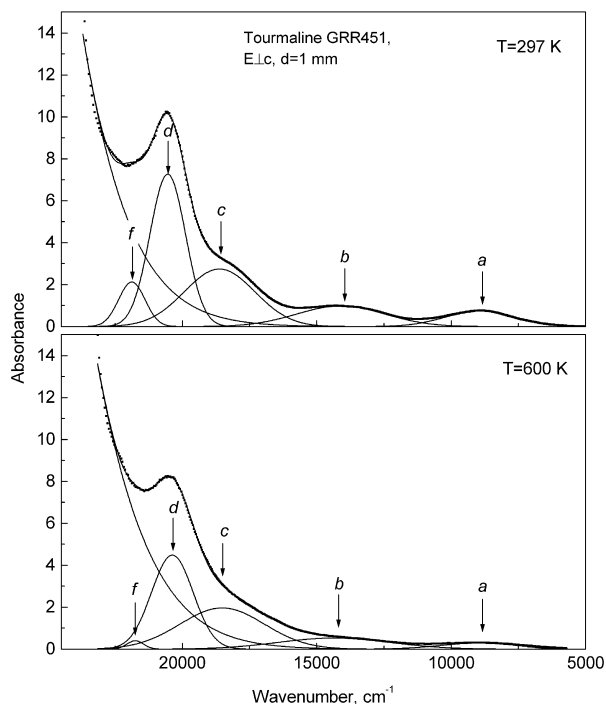


FIGURE 2. Gaussian curve-fitting of the $E_{||c}$ polarized spectrum of ferrian dravite measured at 297 and 600 K.

low temperature (Schugar et al. 1972).

At elevated temperature (Fig. 2, Table 1), both the linear and integral intensities of bands *a* to *d* decrease, whereas their widths increase. The shifts in energies of the bands are not great enough to be determined reliably by the fitting procedure. Band *a* displays the greatest intensity decrease. In the temperature range 300–600 K, its integral intensity decreases by a factor of about 2.2 (Table 1). Integral intensities of bands *b*, *c*, and *d* decrease by factors of ~1.5, ~1.2, and ~1.4, respectively.

Spectra of tourmaline in $E_{||c}$ -polarization, measured at 297 and 600 K (Fig. 3), show that the intensity of the *e* band significantly decreases, whereas the absorption edge increases and shifts slightly to lower energies. The curve fitting (Table 1) shows that the linear intensity of band *e* decreases more than a factor of two but because of broadening, its integral intensity decreases by only a factor of ~1.5. The energy of the band remains almost unchanged.

Spectra of the natural sample measured at three different pressures, 10⁻⁴, 5.44, and 10.51 GPa are shown in Figure 4. As is expected, the spectrum obtained at ambient pressure (10⁻⁴ GPa) using unpolarized light and the plate cut perpendicular to

the *c* axis is nearly identical to the $E_{||c}$ spectrum scanned in polarized light on the plate cut parallel to the *c* axis (cf. Figs. 1 and 4). Minor differences between the two spectra are most probably caused by the different thickness of the samples used in the two experiments (see the experimental section). At $\lambda > \sim 550$ nm, absorption by the thin sample (0.05 mm) used for the high-pressure measurements is so low that it causes a low signal/noise ratio and poor quality of the spectra in this range.

Changing pressure produces large changes in the spectra of this tourmaline sample (Fig. 4). First, intensities of bands *a* and *b* increase by a factor of about 5. The bands shift to higher energy, from ~8930 to ~10400 cm⁻¹ (band *a*) and from ~13 900 to ~14 700 cm⁻¹ (band *b*). The energy separation of the bands decreases from 4970 to 4300 cm⁻¹. Second, the intensity of band *c* decreases with increasing pressure without any evident change in energy so that it almost disappears at pressures between 5.44 and 9.55 GPa. Third, the high-energy edge decreases and shifts to higher energies.

The *d* band does not show such pronounced changes. The intensity of the band increases with pressure, and it shifts from 20 580 to 20 700 cm⁻¹; the band becomes broader and asymmetric, and at least two distinct shoulders at ~21 900 and ~22 700 cm⁻¹ appear on the high-energy wing of the *d* bands. It is not clear whether the appearance of the shoulders is due to the shift of the absorption edge that decreases the overlap of these bands with the absorption edge, or to the intensification of these bands due to changes brought about by compression of the structure.

These changes cause a distinct change of color from orange (in the 0.05 mm thick slice) to grayish-green.

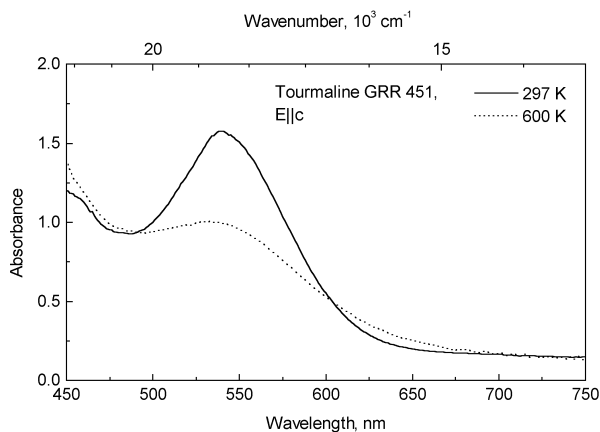


FIGURE 3. $E_{||c}$ spectrum of natural tourmaline measured at 297 and 600 K. The sample thickness is 1.02 mm.

TABLE 1. Results of curve fitting of the optical spectrum of ferrian dravite, measured at 297 and 600 K

Band	Polarization	Energy (ν), cm ⁻¹		Half-width ($\nu_{1/2}$), cm ⁻¹		Linear intensity, cm ⁻¹		Integral intensity, cm ⁻²	
		297 K	600 K	297 K	600 K	297 K	600 K	297 K	600 K
<i>a</i>	($E_{ c}$)	8927	8863	3039	3507	7.4	3.0	24060	11170
<i>b</i>	($E_{ c}$)	14101	14354	3879	4908	9.9	5.3	40700	27830
<i>c</i>	($E_{ c}$)	18613	18516	3092	3708	27.4	19.6	90390	77640
<i>d</i>	($E_{ c}$)	20542	20371	1561	1819	72.6	44.8	120780	86860
<i>e</i>	($E_{ c}$)	18387	18340	2513	3262	12.0	5.9	30360	20450
<i>f</i>	($E_{ c}$)	21879	21750	1158	733	21.0	4.0	26240	3130

Notes: The data for linear and integral intensities are normalized for a thickness of 1 cm.

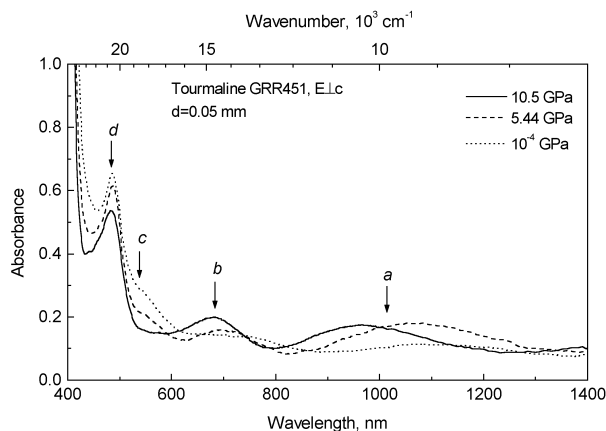


FIGURE 4. Spectra of tourmaline at different pressures. The sample thickness is ~ 0.05 mm.

Synthetic tourmaline

The spectrum of the synthetic Fe^{3+} -bearing tourmaline under ambient conditions is shown in Figure 5. All features attributed to Fe^{3+} in the spectrum of the natural sample (Fig. 1), i.e., bands c , d , and e , occur in the spectrum of the synthetic sample, although with lower intensity. In contrast to the natural sample, in the spectrum of the synthetic tourmaline there is no sign of the Fe^{2+} spin-allowed bands a and b (cf. Figs. 1 and 5). This is evidence that, in the synthetic tourmaline, all iron is in the trivalent state.

The $\text{E}||c$ -polarized e band, which is relatively strong in dravite (Fig. 1), is seen only as a vague weak shoulder superimposed on the absorption edge. The bands in the two NIR ranges, 1350–1500 and 2200–2500 nm, caused by OH vibrations, are essentially the same in both natural and synthetic samples.

The most important difference between the spectra of the natural and synthetic samples is a weak $\text{E}||c$ -polarized band at $\sim 10\,600\text{ cm}^{-1}$, labeled g . This band is distinct in the spectrum of the synthetic tourmaline (Fig. 5) but is not seen in the natural sample (Fig. 1), evidently because of masking interference of the broad and relatively intense c band caused by Fe^{2+} - Fe^{3+} exchange-coupled pairs.

DISCUSSION

In general, the results obtained here from the natural sample are consistent with the previous interpretation of the main features in the spectrum of the red ferric-bearing dravite (Mattson and Rossman 1984).

The temperature and pressure dependencies of the a and b bands (Figs. 2 and 4, Table 1) suggest that they are caused by the spin-allowed dd -transitions ${}^3T_{2g} \rightarrow {}^5E_g$ of $\text{Fe}^{2+}(\text{Y})$ that are enhanced by exchange coupling with neighboring Fe^{3+} ions at adjacent Y sites. Indeed, the inverse temperature-dependence of the intensity of such bands was established in a number of (Fe^{2+} , Fe^{3+})-bearing minerals, including tourmalines (Smith and Strens 1976; Smith 1978; Mattson and Rossman 1987; Taran et al. 1996). Smith (1978) suggested that this increase in intensity may be due to thermal contraction of the structure resulting in increased overlap of the metal-metal orbitals, or alternatively, it

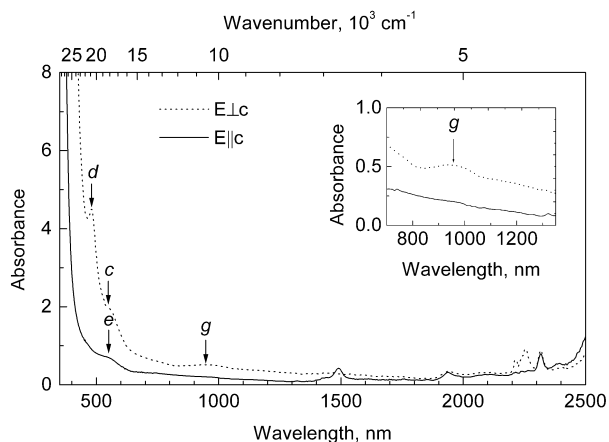


FIGURE 5. Polarized spectra of Fe^{3+} -doped synthetic tourmaline at ambient temperature and pressure. The sample thickness is 0.22 mm. The spectrum is recalculated to a thickness of 1 mm. A part of the spectrum is enlarged in the inset, where the $\text{E}||c$ polarized g band, caused by ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition of Fe^{3+} , is clearly seen.

may be caused by a changing population of excited vibronic states of the electronic ground-state function of (Fe^{2+} , Fe^{3+}) pairs. Note that, at elevated temperature, the intensity of band a decreases more than that of band b (see Results). This observation is consistent with the results of Taran et al. (1996) for (Fe^{2+} , Fe^{3+})-bearing elbaite, in which the rate of temperature variation of band a is more than four times greater than that of band b .

The pronounced intensification of the a and b bands and their shift to higher energy with increasing pressure (Fig. 4) are similar to those found by Taran et al. (1996) for schorl. This intensification is probably caused by shortening of Fe^{2+} - Fe^{3+} distances that increases overlapping of Fe^{2+} and Fe^{3+} orbitals during hydrostatic compression of the structure. Therefore, this high-pressure result supports Smith's (1978) suggestion that the change of intensity of the (Fe^{2+} , Fe^{3+})-pair bands on changing temperature may be due to the thermal expansion/contraction of the structure rather than change of population of vibronic levels of the ground electronic state of the pair.

The shift of the a and b bands (Fig. 4, Table 1) is a result of an enhancement of the crystal-field strength of Fe^{2+} due to decrease of Fe^{2+} -O(OH) distances in the coordination octahedra under compression. This effect is readily observed in high-pressure spectroscopic studies of $3d^N$ -ion bearing minerals (e.g., Abu-Eid 1976; Smith and Langer 1982; Langer et al. 1997). The decrease of the splitting of the a and b bands is evidence that, under hydrostatic compression, the local environment of Fe^{2+} in the tourmaline structure becomes more regular.

A comparatively small shift of the d band to higher energies with increasing pressure (Fig. 4, Table 1) is consistent with its attribution to the ${}^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ transition of Fe^{3+} . According to crystal field theory, the energy of this transition is almost independent of the crystal field strength of Fe^{3+} (Lever 1984). Therefore, a large shift of this band under compression of the structure is not expected. Note that, in accordance with such expectations, a minor high-energy shift of this band was

observed in the high-pressure spectrum of Fe^{3+} in andradite and almost no shift was observed in the epidote spectrum (Taran and Langer 2000). The dv/dP value of the ${}^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ band, $\sim 16 \text{ cm}^{-1}\cdot\text{GPa}^{-1}$, in the andradite spectrum is commensurate with that of the d band, $\sim 11 \text{ cm}^{-1}\cdot\text{GPa}^{-1}$, derived from the spectrum of tourmaline (Fig. 4).

The width of the d band, $\nu_{1/2} \approx 1560 \text{ cm}^{-1}$ at 297 K (Table 1), and its molar absorptivity (ϵ) range, 14 to 31 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (Mattson and Rossman 1984), are much higher than those of other silicate minerals containing "isolated" ferric ions. For example, in the spectra of andradite and epidote, the $\nu_{1/2}$ values of this band, 470 and 820 cm^{-1} , respectively (Taran and Langer 2000), are two to three times less than those of the corresponding band in tourmaline. Furthermore, the ϵ -values for andradite and epidote, 0.01 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and 1.29 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, respectively, are one to three orders of magnitude lower than for tourmaline. For these reasons, and due to a compositional dependence, Mattson and Rossman (1984) attributed band d to the ${}^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ transition of exchanged-coupled pairs of $\text{Fe}^{2+}\text{-Fe}^{3+}$. The $E_{\perp c}$ polarization of the band implies that the pairs are in the Y octahedral trimers of the tourmaline structure.

The relatively weak temperature (Table 2) and pressure dependencies (Fig. 4) of the intensity of the d band differ significantly from the a and b bands of ($\text{Fe}^{2+}\text{-Fe}^{3+}$) exchanged-coupled pairs. This is evidence of the different nature of the two types of bands and the different mechanisms of their intensification. For the Fe^{3+} spin-forbidden bands in $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairs, the intensification is explained by relaxation of the spin-multiplicity selection rule that makes the initially spin-forbidden transitions of Fe^{3+} spin-allowed (e.g., Ferguson and Fielding 1972; Rossman 1988). Behavior comparable to the d band in tourmaline has been observed in the spectrum of natural and synthetic Fe-bearing sapphires. In these spectra, the intensity of the ${}^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$ band, which is also attributed to exchange-coupled $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairs, displays both a relatively weak temperature dependence and noticeable changes of the band shape in the temperature range applied here (Eigenmann and Günthard 1972; Eigenmann et al. 1972; Ferguson and Fielding 1972; Taran and Langer 1998).

There is no theoretical explanation of intensification of the spin-allowed dd bands of Fe^{2+} in $\text{Fe}^{2+}\text{-Fe}^{3+}$ pairs. Therefore, the iron ion-pair phenomena need further experimental and theoretical investigation.

The intensity of the $E_{\perp c}$ -polarized e band decreases at high temperature (Fig. 3, Table 1). Mattson and Rossman (1984) explained a similar temperature behavior of this band in the 83–296 K range by proposing that the band may be caused by a transition involving simultaneous excitation of the (${}^6A_1 \rightarrow {}^4T_1$) transition in both members of $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairs in the Z site helixes of the structure. This type of electronic transition, called a two-exciton transition by Fujiwara et al. (1972), causes "cold" absorption bands that become more intense at low temperature. Calculated from the energy of the e band, the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition of $\text{Fe}^{3+}(\text{Z})$ in the dravite spectrum should occur around 9200 cm^{-1} (1090 nm).

A weak g band, which appears at $\sim 10\,600 \text{ cm}^{-1}$ in the $E_{\perp c}$ -polarized spectrum of the synthetic sample (Fig. 5), is assigned to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition of Fe^{3+} in octahedral coordination

for a number of reasons. First, the composition of the sample, which contains no other transition metal ions but Fe^{3+} (see Results), implies that all bands in the visible and near infrared regions down to $\sim 9500 \text{ cm}^{-1}$, including the g band, are caused by electronic transitions of Fe^{3+} . Second, the energy, $\sim 10\,600 \text{ cm}^{-1}$, and relative intensity of the g band are typical of the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition of ${}^{60}\text{Fe}^{3+}$ in oxygen-based minerals (e.g., Rossman 1975, 1976; Burns 1993; Taran and Langer 2000). The half-width, $\nu_{1/2}$, is difficult to determine because of the low intensity of the band in question (Fig. 5) and, thus, of the low signal/noise ratio in the range under consideration. By curve fitting, $\omega_{1/2}$ may vary, depending on choice of the background simulation, from ~ 1300 to $\sim 2000 \text{ cm}^{-1}$.

Taking into account the similarities between spectra of the natural and synthetic tourmaline (cf. Figs. 1 and 5) and the structure-refinement results of Hawthorne et al. (1993) for the natural sample, it is reasonable to assume that in the synthetic tourmaline, Fe^{3+} occurs primarily at the Y site. Accepting that the energy of the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition of $\text{Fe}^{3+}(\text{Y})$ is $\sim 10\,600 \text{ cm}^{-1}$, one can predict that the energy of the two-exciton transition $2 \times ({}^6A_{1g} \rightarrow {}^4T_{1g})$ of a $\text{Fe}^{3+}(\text{Y})\text{-Fe}^{3+}(\text{Y})$ pair in the tourmaline structure is $\sim 21\,200 \text{ cm}^{-1}$. This is appreciably greater than the energy of the e band, $\sim 18\,400 \text{ cm}^{-1}$ (Table 1).

Because the Z octahedron is smaller than the Y octahedron (mean Z-O and Y-O distance is 1.929 Å and 2.025 Å, respectively, Burns 1993), crystal field theory (Lever 1984) predicts that the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition of Fe^{3+} at the smaller Z site should occur at a lower energy than that of $\text{Fe}^{3+}(\text{Y})$. From this point of view, the energy of the two-exciton transition $2 \times ({}^6A_{1g} \rightarrow {}^4T_{1g})$ of the $\text{Fe}^{3+}(\text{Z})\text{-Fe}^{3+}(\text{Z})$ pair should be lower than 21 200 cm^{-1} . The energy of the e band, $\sim 18\,400 \text{ cm}^{-1}$, fits this condition and, presumably, is caused, as assumed by Mattson and Rossman (1984), by the $2 \times ({}^6A_{1g} \rightarrow {}^4T_{1g})$ electronic transition of an $\text{Fe}^{3+}(\text{Z})\text{-Fe}^{3+}(\text{Z})$ pair. Such an assignment is consistent with the $E_{\perp c}$ -polarization of the band and the strong temperature dependence of its intensity (Mattson and Rossman 1984). Note that by the strong temperature dependence of intensity, the band e significantly differs from "ordinary" spin-forbidden dd bands of "isolated" octahedral Fe^{3+} in, for instance, andradite and epidote (Taran and Langer 2000). This fact also is evidence that the e band is caused by an exchange-coupled pair interaction rather than an "ordinary" dd transition of Fe^{3+} .

Note that, according to Hawthorne et al. (1993), Fe^{3+} in natural ferric dravite occurs at the Y site. Probably only a small fraction of ferric ions enter the Z positions, and only some of them form exchange-coupled $\text{Fe}^{3+}(\text{Z})\text{-Fe}^{3+}(\text{Z})$ pairs responsible for the "cold" e band in spectra of both natural and synthetic tourmalines. Although the synthetic tourmaline has a higher Fe^{3+} -content than the natural tourmaline, 0.61 and 0.53 apfu, respectively, the intensities of the absorption edge and the c , d , and e bands in the former are significantly lower than in the latter (cf. Figs. 1 and 5). This suggests that, in the natural tourmaline, degrees of $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairing at both the Y and Z sites are higher than in synthetic tourmaline. We speculate that a possible cause may be the different rate and temperature of crystallization of the natural and synthetic samples.

Due to the features of the high-pressure technique used in the present study the pressure dependence of the $E_{\perp c}$ -polarized

e band cannot be measured. Because of the low intensity of the absorption spectrum of the synthetic tourmaline, the latter cannot be measured at high pressures either.

The decrease in wavelength of the high-energy absorption edge and, especially, the decrease in intensity and subsequent disappearance of the *c* band at high pressure (Fig. 4) are rather unusual phenomena. So far, mainly the pressure-induced intensification and, rarely, the appearance of new absorption bands caused by electronic transitions of $3d^N$ -ions, have been reported (Burns 1993; Taran et al. 1996; Taran and Langer 1998). Only recently, in the spectrum of a Co-bearing synthetic garnet, was a pressure-induced disappearance of a presumed spin-forbidden *dd* band of $^{[VIII]}Co^{2+}$ observed (Taran et al. 2002).

The pressure-induced decrease and subsequent disappearance of the *c* band, previously assigned to Fe^{3+} - Fe^{3+} pairs (Mattson and Rossman 1984), is difficult to explain, especially in view of the fact that the *d* band, which is also caused by Y site Fe^{3+} - Fe^{3+} pairs, noticeably increases as a function of pressure.

Indeed, shortening of interatomic distances under hydrostatic compression most probably increases orbital overlap of neighboring atoms in the structure. Because of this the value of the exchange integral, which is responsible for the pair effects in Fe^{3+} - Fe^{3+} pairs (Ferguson and Fielding 1972), should increase. Therefore, one may expect that the bands, which originate from the exchange interaction, should intensify at higher pressures.

The decrease in the intensity of the *c* band may be connected to the simultaneous decrease in the intensity of the absorption edge. At the moment we can only state that the probability of the electronic transition that gives rise to the *c* band decreases when tourmaline is compressed. This may be caused by an increased regularity of the crystal field of $Fe^{3+}(Y)$ under hydrostatic compression.

The ultraviolet absorption edge is most probably caused by an oxygen- Fe^{3+} charge-transfer transition, the pressure dependence of which is not yet studied in detail. Usually, in the spectra of iron-bearing crystals, the absorption edge caused by this type of transition shifts to lower energy with increasing pressure (Burns 1993). Possibly, the high-energy shift of the edge in the tourmaline studied here indicates that besides "isolated" ferric ions, the edge is partly caused by exchange-coupled pairs of Fe^{3+} . The fact that, in the natural sample which contains smaller amount of Fe^{3+} than the synthetic sample, the edge is considerably stronger (Figs. 1 and 5), is consistent with this hypothesis.

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