

### 8.1.3.5 Tourmaline family of silicates

The silicates from the tourmaline family are listed in Table 1. The classification made by [99H1] was used for the tourmaline group. In addition, according to [91N1], the silicate verplanckite was added to this group.

#### 8.1.3.5.1 Crystal structures. Lattice parameters

The most important boron containing silicates, tourmalines, exhibit a quite complex crystal chemistry because of the presence of trigonal (B site), tetrahedral (T site), octahedral (Y, Z sites) and polyhedral (X site) cation sites. The chemical formula of tourmalines may be written as  $XY_3Z_6[T_6O_{18}](BO_3)_3V_3W$ . Ignoring the trace constituents, the compositions may be described by: X = Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, □; Y = Li<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, Fe<sup>3+</sup> (Ti<sup>4+</sup>); Z = Mg<sup>2+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, V<sup>3+</sup>, Cr<sup>3+</sup>; T = Si<sup>4+</sup>, Al<sup>3+</sup> (B<sup>3+</sup>); B = B<sup>3+</sup>; V = OH<sup>-</sup>, O<sup>2-</sup> [O3]; W = OH<sup>-</sup>, F<sup>-</sup>, O<sup>2-</sup> [O1]. The elements in parantheses are only expected to occur at these sites. By □ is denoted a vacancy.

According to [99H1] the tourmalines can be classified according to X-site occupancy (Na,K); Ca or □) into three principal groups: (1) **alkali tourmalines** (Na+K dominant at X); (2) **calcic tourmalines** (Ca dominant at X); **X-site vacant tourmalines** (□ dominant at X) – Table 1. These groups are further divided, initially based on the W-site occupancy, then by the (actual or inferred) V-site occupancy, next by the (actual or inferred) Y-site occupancy, and finally by the (actual or inferred) Z-site occupancy. In [99H1] the names and compositions of tourmalines were analyzed and some new end-members were proposed. Thus, in the following we used this classification instead of that given by [91N1].

The structure of tourmaline was a matter of debate in the earlier investigations [48H1, 49B1, 50B1, 51I1]. Only the model of [48H1] has been accepted and most subsequent studies were based on this model. Structure refinement was performed on different tourmalines [62B1, 69B1, 71T1, 72D1, 75F1, 79N1, 81N1, 82G1, 84S1, 93H1, 93M1, etc.]. As example, the lattice sites in case of dravite are listed in Table 2 [93H1]. The [XO<sub>9</sub>] polyhedron is formed by six bridging oxygens: three O4 and three O5 in the [Si<sub>6</sub>O<sub>18</sub>] ring, and three oxygens O2 belonging to the triad of Y octahedra. The X-site is filled with alkali ions, mainly Na<sup>+</sup>, less frequently Ca<sup>2+</sup>, and can be also vacant. The [TO<sub>4</sub>] tetrahedral site, representing the independent unit of the [T<sub>6</sub>O<sub>18</sub>] ring, is formed by 4 oxygens: O4, O5, O6, O7. The O4 and O5 are bridging oxygens belonging to the [T<sub>6</sub>O<sub>18</sub>] ring, while O6 and O7 link each tetrahedron with the underlying octahedral portion. The T site is occupied by (90...100) % Si [99P1]. It is accepted that if silicon is deficient, Al can occupy the T site. Some authors assume also the presence of Ti<sup>4+</sup> and B<sup>3+</sup> in this site, at the amount, above 3 apfu for the latter [81P1, 93G2]. The B structural site is filled almost exclusively with B<sup>3+</sup> ions. Some authors [79S2] observed a deficit of this element and suggested the need of its compensation with Al<sup>3+</sup> ions. The deficit of boron is often small (< 0.03 apfu). In last years the amount of boron is stoichiometrically fixed at 3.0 apfu [99P1]. For this reason, the B site was generally characterized with parameters describing the geometry of the BO<sub>3</sub> group involving three oxygens: one O2 and two O8. Besides boron, there are X and Y ions in the nearest neighbourhood of O2, while around O8 only Z ions. An almost regular arrangement of boron ions in the structure of tourmalines was reported [99P1]. The octahedral portion (Fig. 1b) consists of three Y octahedra, linked along the O1–O2 edges, and six Z octahedra attached to them along the O3–O6 edges (two of them to each Y octahedron). Each Z octahedron is additionally linked along the O7a–O8 and O7b–O8a edges with two adjacent Z octahedra situated above (+1/3c) and below (–1/3c) it. As a result of such a linkage, in the structure of tourmaline there are spiral chains of Z octahedra around the 3<sub>1</sub> axis [99P1]. The chains are parallel to the crystallographic c-axis [99P1]. In earlier studies it was generally assumed that if Al exceeds 6 apfu, it fills completely Z octahedra. In this case, any excess of Al was attributed to Y octahedra. But, by spectroscopic investigations was assumed a disordered distribution of divalent ions and aluminium between Y and Z sites. Later on, the geometrical deformations of coordination polyhedra were analyzed [89A1, 89F1]. In [93H1] a linear relationship was considered between mean sizes of coordination polyhedra and mean radii of complex ions in various silicates including tourmalines. Based on the hard-sphere model, the Mg,Al-disorder was discussed for the crystal structure of dravite. The same assumptions were used in analyzing the crystal structures of tourmalines [93G1, 94B1, 95M1, 96H1]. The part played by the substitutions in adjacent cation sites was emphasized [95M1, 95U1, 99P1]. In [99P1, 00P1] the mean sizes of X, Y, Z, B and T sites were modeled as well as the unit-cell parameters of tourmalines on the basis of their chemical compositions, by using relations between the mean bond lengths in coordination polyhedra and cation populations in these sites. The statistical analysis of the relationship of the lattice parameters versus mean bond

lengths of the X, Y, Z, B and T polyhedra indicates that the  $a$  parameter depends significantly on sizes of all the mentioned sites, while in the case of the  $c$  parameter the effect of the B site is structurally negligible [99P1]. For both parameters, the decisive role of the sizes of octahedral sites can be explained by geometrical relationships resulting from the presence of the network of mutually linked Y and Z octahedra. The unusually strong effect of mean sizes of Z octahedra on the  $c$  unit-cell parameter, described by the relation  $A+BdZ$  [89A1, 90K1], was associated with the existence in the structure of tourmalines of spiral chains of Z octahedra arranged around the  $3_1$  axis, parallel to the  $z$  crystallographic axes [99P1]. The lack of a statistically significant effect of the B site on the  $c$  parameter was associated to the arrangement of the  $BO_3$  triangle in the tourmaline structure almost parallel to the (001) plane [99P1].

The Y octahedral sites are determined by 4 oxygens (two O2 and two O6) and O1 and O3 sites filled with  $(OH)^-$  or  $F^-$  or, after deprotonization, of one or both structural sites, also by oxygen. The Y sites are filled mainly with divalent ions or the heterovalent combination  $Al+Li$ , and then the O1 and O3 sites are occupied by  $OH^-$  and  $(OH/F)^-$  ions, respectively, or with trivalent ions (Al, Fe, Cr, V) and  $Ti^{4+}$ , resulting then in the occupation of the O1 and O3 sites by oxygen [99P1]. The Z tetrahedral site has in neighbourhood 5 oxygens: O6, O7a, O7b, O8, O8a and O3 site with  $OH^-$  group or oxygen after deprotonization of this site. The Z octahedra are filled mainly with aluminium and when there is a deficit of this element, also with  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Ti^{4+}$ . In uvite or feruvite (hydroxy feruvite), the Z sites are occupied by divalent cations prevalently  $Mg^{2+}$  or  $Fe^{2+}$ .

In tourmaline structure there are two sites  $V = O3$  and  $W = O1$  that are occupied by monovalent anions  $OH^-$  and  $F^-$  or by the divalent anion  $O^{2-}$ . The  $(OH + F)$  can be less than 4.0 apfu with the deficiency being made up by  $O^{2-}$  [81P1, 86P1, 94D1, 95T1]. The V and W sites are crystallographically distinct and the constituent anions  $OH^-$ ,  $F^-$  and  $O^{2-}$  order differently over these sites [99H1]. The V (O3) site in tourmaline is dominated by  $OH^-$ , but can be occupied also by  $O^{2-}$ . In [93G1] was argued that tourmalines containing both  $O^{2-}$  and  $OH^-$  at the V/W sites will preferentially show partition of  $OH^-$  at the V site. They noted that buergerite is the exception, with  $O^{2-}$  dominantly at the V site. Among the current end-members, the other exception is olenite. Consequently, the V site can be considered to be a binary  $(OH^-O^{2-})$  differing with  $OH^-$  more commonly preferred at this site unless the Y and Z sites are completely occupied by trivalent cations (e.g. buergerite and olenite) [99H1]. In the W site,  $F^-$  is ordered completely at this site [93G1, 95M1]. This site, commonly, also contains  $OH^-$  and  $O^{2-}$  [96H1]. Thus, the W site can be considered as to make a subdivision of primary tourmalines into secondary hydroxy-, fluor- and oxy-end-member subgroups [99H1]. When  $O^{2-}$  is dominant at the W site, short range ordering is commonly required at the Y and Z sites in order to satisfy local bond-valence and bond-length requirements [96H1].

The site occupancies in tourmalines were analyzed [71T1, 75F1, 77F1, 79N1, 81P1, 84N1, 84S1, 86P1, 86S2, 88G1, 89G2, 90L1, 93G1, 93G2, 93H1, 94B1, 94D1, 95M1, 96H1, 99H1, etc.]. Extensive substitutions in the Y, Z octahedra and in the large cation sites X give rise to tourmaline solid solutions with variable compositions [77F1, 88G1, 90L1, 93M1, 93T1]. According to [93H1] in dravite<sup>5)</sup> (for composition see footnote in Table 3) there is no significant transition metal occupancy of the Z-site. Al in excess of that necessary to fill the Z site, was assigned to Y. When the amount of Al is insufficient to fill the Z site, the deficiency can be made by transition metals [75F1, 79N1] and Mg [89G2]. The analysis of cation ordering between Y and Z octahedral sites, in the schörl-dravite series, suggest that the occurrence of an  $Fe^{2+}$  cation on a Y octahedral site may be locally associated with the absence of Mg at both of the neighbouring Z sites, as substitutions of  $Fe^{2+}$  on Y and Mg on Z require antithetic shifts of the O6 anion [99B1]. In buergerite<sup>13)</sup> a substitution of Fe into Al(18c) site was found [71T1]. In fohsite, the refinement shows the low occupancy of X site and the dominantly divalent state of Fe at the Y site [93M1]. In [96H1] was noted that the presence of  $O^{2-}$  at the W site influences the occupancy of the Y site due to local bond valence and bond length requirements. In Li-free tourmalines with  $O^{2-}$  at the W site, the stable configuration at the Y-site is either  $(M^{2+} + 2M^{3+})$  or  $3M^{3+}$  where M denotes a cation. These short-range order configurations at the Y site result in disordering such that Mg is displaced to the Z site and Al to the Y site [99H1]. For the Li-bearing tourmalines, where a monovalent anion is at the W site, the stable cation configuration is  $(Li + 2Al)$  or  $(2Li + Al)$ . The former configuration occurs in rossmanite and the latter in liddicoatite. In end-member elbaite, equal amounts of each of these two configurations are likely. In Li-bearing tourmalines, bond valence and bond-length requirements imply that  $OH^-$  can only be replaced by  $O^{2-}$  to a limited extent, possibly 25 % [99H1]. The Z-site is occupied dominantly by trivalent cations, most commonly by Al. Among the current end-members, chromdravite and povondraite, have  $Cr^{3+}$  and  $Fe^{3+}$ , respectively, as the dominant occupant of the Z-site. In the X-site vacant and alkali-tourmaline end-members, Al is the only trivalent cation to occupy the Z site –. In the calcic tourmalines, uvite and hydroxy-feruvite, the Z site is occupied by  $Al_5Mg$ , whereas liddicoatite has  $Al_6$  at Z – Table 1. If  $O^{2-}$  is dominant at the W site, additional combinations are

possible produced by disordering reactions induced by short-range ordering requirements of the anions coordinating the Y site [96H1, 99H1]. The presence of  $\text{Mn}^{2+}$  ions in tourmalines was analyzed [29K1, 61S1, 84N1, 84S1, 86S2, 94B1, 99H1] mainly in connection with possible Mn end-members. According to [99H1] possible end-members are: “Mn-dravite”,  $\text{NaMn}^{2+}_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$ ; “Mn-foitite”,  $\square\text{Mn}^{2+}_2\text{AlAl}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$ ; oxy-Mn-dravite,  $\text{NaMn}^{2+}_2\text{AlAl}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$  and “oxy-Mn-foitite”,  $\square\text{Mn}^{2+}\text{Al}_2\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$ . It was shown [99H1] that the composition given by [94B1] extends along the elbaite – “Mn-dravite”. The tourmaline reported by [86S2] shows some solid solution toward “Mn-foitite” and was suggested as the appropriate end-member composition “Mn-dravite” another potential end-member for a  $\text{Mn}^{2+}$ -dominant tourmaline [99H1]. The vanadium bearing tourmaline was also studied [79F1].

The studies on boron contents in tourmalines yielded different results for different tourmaline species. Structural studies of Mg-rich tourmalines show that B contents are close to stoichiometric composition with no evidence for  $^{10}\text{B}$  [95M1, 95T1, 99B1, 01E1]. Also no  $^{10}\text{B}$  was detected by  $^{11}\text{B}$  MAS NMR in Mg-rich tourmaline (dravite) [97W1, 99T1, 00S1]. Compositions containing excess boron have been also reported [69B1, 80S2, 94D1, 97E1, 97W1, 98D1, 01W1]. In [69N1] by using EPR measurements, evidence was obtained for the substitution of silicon by boron at the tetrahedral site in elbaite (0.0006 B apfu). In [80S2] was proposed that excess boron is accommodated not only at the trigonal sites, but also at tetrahedral sites. In [97E1] the crystal structure of olenite was refined with 4.225 B and 4.871 Si apfu and the data were interpreted by the substitution of Si by B [96H1]. In [00H1] the presence of approximately one  $^{10}\text{B}$  per six membered ring was demonstrated confirming the work of [97E1]. In [97W1, 00S1, 01W1] olenites were synthesized with an even greater amount of excess boron and boron substitution for silicon, and cited  $^{11}\text{B}$  MAS NMR showed evidence for the presence of both trigonal and tetrahedral boron. The crystal structure studies of Al-rich and Li-bearing natural tourmalines (olenite, elbaite) showed that B substitutes for Si to significant amount at the tetrahedral site [00H1, 01H1].  $^{11}\text{B}$  MAS NMR spectroscopy study of Al- and Li-rich natural tourmaline [99T1] showed the presence of  $^{10}\text{B}$ . The synthesis of  $^{10}\text{B}$  bearing tourmalines determined the  $p$ - $T$ - $x$  conditions necessary for this substitution to occur [97W1, 01W1]. Thus, by high-pressure experiments, an excess boron olenite was obtained having as much as 38 % of the tetrahedral silicon replaced by boron [00S1]. Other studies [00M1, 02M1] on different synthetic Al-rich tourmalines support also the above investigation. In [01H1] was shown that tourmalines with excess of  $^{10}\text{B}$  discovered to date contain essentially no Mg.

In the following, the composition features which were used for classification of tourmalines and the reasons for proposing new names for the end-members of this group are reviewed [99H1]. In **alkali tourmalines**, the X site is occupied mainly by Na(K). The  $\text{Y}_3$  position in **elbaite** end-member is occupied by  $\text{Li}_{1.5}\text{Al}_{1.5}$  and in **dravite** and **chromdravite** by  $\text{Mg}_3$ . In dravite the  $\text{Z}_6$  site is occupied by Al and in chromdravite by Cr. In mineral **schörl** the  $\text{Y}_3$  is occupied by  $\text{Fe}^{2+}_3$  and in **buergerite** by  $\text{Fe}^{2+}_3$ . The end member composition of **foitite** was given with variable occupancy at the Y site:  $\text{Y}_3 = \text{Fe}^{2+}_2(\text{Al}, \text{Fe}^{3+})$  [93M1]. As Al is dominant over  $\text{Fe}^{3+}$  in the formula of the holotype, for the end member Y composition was considered  $\text{Fe}^{2+}_2\text{Al}$  [99H1]. **Olenite** was initially defined as  $\text{Na}_{1-y}(\text{Al}_{3-x}\text{Li}_x)\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3[\text{O}_{3-2x-y}(\text{OH})_{1+2x+y}]$  with  $y = 0 \dots 1$  and  $x = 1.50 \dots 0.75$ , having the ideal formula  $\text{Na}_{1-x}\text{Al}_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{O}, \text{OH})_4$  with  $x = 0 \dots 1$  [86S1]. According to [99H1] the latter composition was found to be unsatisfactory as there are several constituents (Na, O, OH) that are considered as variables. The corresponding end-member is given in Table 1. The most Al-rich composition, reported for olenite, is:  $(\text{Na}_{0.51}\square_{0.43}\text{K}_{0.01}\text{Ca}_{0.05})(\text{Al}_{2.91}\text{Mn}_{0.10})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{O}_{2.57}\text{OH}_{1.44}\text{F}_{0.03})$  [86S1]. The structural formula of holotype **povondraite** was given as [93G2]:  $(\text{Na}_{0.80}\text{K}_{0.26})(\text{Fe}^{3+}_{2.28}\text{Fe}^{2+}_{0.27}\text{Mg}_{0.53})(\text{Fe}^{3+}_{4.29}\text{Mg}_{1.36}\text{Al}_{0.32})(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_{3.12}\text{O}_{0.88}$  and the ideal end-member formula as  $\text{NaFe}^{3+}_3\text{Fe}^{3+}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{O}, \text{OH})_4$ . According to [99H1], the above is not the end member formula because the V and W contents were written as variable. In the holotype formula the dominant trivalent cation is  $\text{Fe}^{3+}$  and the dominant divalent cation is  $\text{Mg}^{2+}$ . Therefore the formula with  $\text{Na} \equiv (\text{Na} + \text{K})$ ,  $\text{Fe}^{3+} \equiv (\text{Fe} + \text{Al})$  and  $\text{Mg}^{2+} \equiv (\text{Mg}^{2+}, \text{Fe}^{2+})$  may be written  $\text{Na}(\text{Fe}_{2.28}^{3+}\text{Mg}_{0.80})(\text{Fe}_{4.61}^{3+}\text{Mg}_{1.36})(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_{3.12}\text{O}_{0.88}$  with the ideal end member  $\text{NaFe}_3^{3+}(\text{Fe}_4^{3+}\text{Mg}_2)(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{O}$ . All sites except the Z site are completely ordered. A survey of ferrian tourmalines shows compositional trends consistent with this ideal end-member composition [99H2].

The **calcic tourmalines** are listed in Table 1 [99H1]. In [29K1] the ideal composition of **uvite** was defined as  $\text{H}_8\text{Ca}_2\text{Mg}_8\text{Al}_{10}\text{Si}_{12}\text{B}_6\text{O}_{62}$  which was rewritten as [77D1]:  $\text{CaMg}_3(\text{Al}_5\text{Mg})(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_4$ . The ideal composition of feruvite was defined as  $\text{CaFe}_3(\text{Al}, \text{Mg})_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_4$  [89G2]. According to [99H1] this is

not a true end-member and is not adequate as the valence state of Fe is not specified. Refinement of the structure shows that all Fe at the Y site is in the divalent state and that the Z site is  $(\text{Al}_{4.72}\text{Fe}_{0.34}^{3+}\text{Mg}_{0.82}\text{Fe}_{0.12}^{2+})$  which is close to  $(\text{Al}_5\text{Mg})$ . Thus, according to [99H1] the end-member was named as **hydroxy feruvite** and was written as  $\text{CaFe}^{2+}_3(\text{Al}_5\text{Mg})\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{OH}$ . The ideal composition of **liddicoatite** was given as  $\text{Ca}(\text{Li},\text{Al})_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{O},\text{OH})_3(\text{OH},\text{F})$  and the end-member composition  $\text{Ca}(\text{Li}_{1.74}\text{Al}_{1.26})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3[(\text{OH})_{2.48}\text{O}_{0.52}](\text{F},\text{OH})$  [77D2] with the proviso that this is not a pure end-member. Analyzing the composition, it was concluded [99H1] that the end-member is  $\text{Ca}(\text{Li}_2\text{Al})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{F}$ . In addition, any O at W and V sites should be assigned to W (the O1 site) [96H1] in the formula derived from the analysis of [77D2].

The **X-site vacant** tourmalines were studied. Tourmalines in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  were synthesized [78W1, 79R1, 84W1, 85R1]. In [84W1, 01W1] presented evidence for tourmalines having vacant X-site. Tourmalines in which Mg partially to completely occupies the X-site were also reported [85R1]. The name of “alkali free dravite” was used [96W1]. A ferrous analogue of the above X-site vacant synthetic MgAl-tourmaline was defined and named **foitite** [93M1]. Thus, natural foitite was classified in the X-site vacancy group [99H1]. Consequently, natural Mg-dominant X-site vacant tourmaline was called **magnesio-foitite** [99H1]. An X-site vacant tourmaline related to the Li-bearing tourmaline elbaite was described [98S1] and named **rossmanite**. Thus, the elbaite described by [66E1] with a total X-site occupancy of 0.22 was actually a rossmanite. The analysis of compositions shows that the X-site vacant tourmalines contain the above three minerals – Table 1 [99H1]. In case of **foitite**, the end-member composition was given with variable occupancy at the Y-site ( $\text{Y}_3 = \text{Fe}^{2+}_2(\text{Al},\text{Fe}^{3+})$ ) [93M1]. In [99H1] was shown that since Al is dominant over  $\text{Fe}^{3+}$  in the formula of the holotype system, the Y-site composition of the end-member is  $\text{Fe}^{2+}_2\text{Al}$ .

In the tourmaline group of silicates also **verplanckite** was included as suggested by [91N1], although this is not included in the classification given by [99H1].

In [75F1] was shown that significant differences existed in the fractional atomic coordinates in tourmalines with large compositional ranges, indicating that single crystal X-ray structural determinations of tourmaline were only valid for the studied sample. In a high-resolution transmission electron microscopy (HRTM) study, [73I1] reported two different plane groups symmetries for buergerite and elbaite. Buergerite showed p31m plane group symmetry, while Fe-bearing elbaite showed p3m1 one. This is unusual since the latter is not compatible with X-ray diffraction for an space group R3m projected down to the *c*-axis. The p31m symmetry in buergerite was not fully confirmed since local perturbations result in p3m1 and “pseudo-hexagonal” p6 plane group symmetry. In [73I1] was argued that the local perturbations of symmetry in buergerite could be explained with medium range-ordering caused by diffusion during electron microscopy runs. They also admitted that the extent of diffusion needed for symmetry observed in Fe-bearing elbaite cannot be explained by simple cation diffusion induced by electron beam irradiation. This matter was further analyzed by [93F1]. Experimental HRTM study confirmed that tourmaline exhibits different [001] plane group symmetries. Unlike [73I1] there have not been observed two different plane group symmetries but four [93F1]. Fe-poor elbaite has p31m symmetry, while Fe-bearing elbaite shows p3m1 one. Elbaite shows p6 symmetry, while Fe–Mg–Al bearing tourmaline has a “pseudo” p6 type of symmetry. Symmetries p3m1 and p6 are not compatible with the space group R3m assigned to tourmaline from X-ray structural determinations. The perturbations of symmetry from p31m to p6 and “pseudo” p6 depend on the magnitude of the scattering amplitude of atoms occupying the 3a and 9b sites. Computer simulations of schörl, elbaite and dravite show different projected potentials for images down the *c*-axes. This supports the observations that the fractional atomic coordinates of tourmaline change with composition [59D1, 75F1]. Regions with high mean concentration of light or heavy elements, a few unit cells apart, are common in Fe-poor elbaite. This results in a marked difference of the distribution contrast in the HRTM image of elbaite. The above data, correlated with  $^{57}\text{Fe}$  NGR spectra, indicate that the composition controls the symmetry,  $^{57}\text{Fe}$  NGR hyperfine parameters and atomic coordinates in tourmaline.

The structure **verplanckite** can be described as a three-dimensional framework composed of four-membered rings,  $(\text{Si}_4\text{O}_{12})^{8-}$  of silicate tetrahedra – Fig. 2 – and of triple units of square pyramidal coordination polyhedra around the X sites which are randomly occupied by Mn, Ti and Fe [73K1]. Three square pyramids are joined at the common apical oxygen atom, Oh4. These triple units are connected to each other in the *c*-direction by silicate rings. Each triple unit and the adjoining silicate tetrahedra (halves of three rings) form a slab of triangular cross-section parallel to the *c*-direction – Fig. 2. The triangular slabs are arranged in chinese checkerboard fashion thus leaving a void of hexagonal cross-section between them. The walls of the void are lined with Ba atoms which are

coordinated to the silicate oxygen atoms and to the Cl1 atoms which are located halfway between the triple units, and to atoms Cl2 and Cl3 in the large hexagonal void. The coordination around Ba1 is formally twelvefold and around Ba2 elevenfold. Since the Cl2 and Cl3 sites are only partially occupied the effective coordination numbers are smaller.

The lattice parameters for tourmalines are listed in Table 3.

The elastic constants for some tourmalines as well as elastic moduli were analyzed [50B2, 50M1, 78H1, 79O1, 85T1, 87T1]. Some values are listed in Tables 4 and 5. The analysis of elastic wave velocities and elastic constants of tourmaline samples indicate [87T1]: (1) partial substitution of Al by Fe in the structure decreases the shear wave velocities; (2) replacement of Na by Ca increases the resistance of the structure against shear deformation involving  $c_{66}$ ; (3) replacement of Al by Mg seems to decrease the resistance of the structure against longitudinal deformation involving  $c_{33}$ . Elastic constants  $c_{11}$ ,  $c_{33}$ ,  $c_{44}$  and  $c_{66}$  of samples studied by [87T1] differ by 1.7...6.7 % indicating that the large differences (up to 21 %) between the values reported by different authors cannot be explained in terms of chemical composition alone.

For crystal structure of tourmalines in earlier stages of studies see also [50D1, 64M1, 66D1].

### 8.1.3.5.2 Magnetic properties

The first magnetic study on tourmalines with iron content from 0.3 to 13.8 wt % evidenced that the susceptibilities, at RT, increase from  $12 \cdot 10^{-6}$  to  $31 \cdot 10^{-6}$  emu/g when increasing the Fe concentration [54K1]. Then, their magnetic properties were analyzed in more detail [67D1, 70T2, 71T2].

In tourmalines, the magnetic ions occupy predominantly Y sites and, in smaller amounts, Z sites. The Y sites, as mentioned in section 8.1.3.5.1, form magnetically isolated equilateral triangles [50B1, 50D1, 51I1, 62B1]. The lengths of the sides of the triangles are  $\cong 3.185$  Å, as determined in buergerite<sup>35)</sup> (for composition see footnote of Table 3). Insofar, as there is only short-range order within the triangles and no significant long-range order between triangles, no magnetic transitions are expected. In addition to the two nearest neighbour Y-sites in the triangle, each Y-site has two nearest neighbour Z-sites at a distance of  $\cong 3.2$  Å. Each Z-site has one nearest neighbour Y-site at  $\cong 3.2$  Å and also four neighbouring Z-sites at an average distance of  $\cong 3.6$  Å. It was expected that the exchange couplings take place between these nearest neighbours pairs. There are exchange interactions for YY, ZZ and YZ nearest neighbours which can be described by  $J$ ,  $J'$  and  $J''$ , respectively. Since, in a first approximation, most  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions are expected to be located on Y-sites, there are isolated three, two or single magnetic ion systems. Since in buergerite<sup>35)</sup>, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio is very high, the  $\chi$  values are primarily determined by  $\text{Fe}^{3+}$  ions ( $3d^5$  configuration). There are large distortions from octahedral symmetry of the environment about Y and Z-sites and thus the orbital degeneracy of  $\text{Fe}^{2+}$  ions is removed. At room temperature and below, only the ground state is populated and in this case the spin-only behaviour with  $S = 2$  for  $\text{Fe}^{2+}$  is expected [71T2].

In [71T2] the temperature dependences of the magnetic susceptibilities were analyzed starting for a Heisenberg exchange interaction Hamiltonian. In case of buergerite<sup>35)</sup>, in a first approximation, all  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions were supposed to be randomly distributed on Y-sites, with the probabilities  $p_1$ ,  $p_2$  and  $p_3$  for  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and nonmagnetic ions, respectively. When considering three  $\text{Fe}^{3+}$  ions on the same triangle, for external field  $H = 0$ , their spins  $S_1$ ,  $S_2$  and  $S_3$  couple together to form the total angular momentum  $S$  with  $S = 1/2, 3/2, \dots, 15/2$ , the degeneracies  $g_S$  being 2, 4, 6, 5, 4, 3, 2, respectively. The relative energy for the state is  $JS(S + 1)$ . In the presence of an applied field, the susceptibility of each level  $S$  is given by the spin-only formula, hence the contributions of all triangles with three  $\text{Fe}^{3+}$  ions to the molar susceptibility are expressed by [71T2]:

$$\chi_m = (3)(p_1^3)(N\mu_0 g^2 \mu_B^2 / 3k_B T) \sum_S g_S S(S+1)(2S+1) \exp\{-JS(S+1)/k_B T\} \cdot \sum_S g_S (2S+1) \exp\{-JS(S+1)/k_B T\} \quad (1)$$

The factor (3) has been included because each mole contains  $3N$  Y-site triangles.

The calculations were repeated for all possible configurations of the triangle ( $2\text{Fe}^{3+}+\text{Fe}^{2+}$ ,  $2\text{Fe}^{3+}+\text{nonmagnetic ions}$ , etc.). The calculated susceptibility depends on only one parameter,  $J$ .

The temperature dependence of the reciprocal susceptibility for buergerite<sup>35)</sup> is shown in Fig. 3a [71T2]. The calculated values, by using  $J/k_B = 7.5$  K are plotted by a solid line. The agreement is good except for the temperature region  $T < 50$  K. In order to take into account also the low-temperature range, it was assumed that

90 % and 10 % of the magnetic ions are distributed in Y and Z sites, respectively. Then  $\cong 75$  % of the Y- and 4 % of the Z-sites are occupied by magnetic ions. In this case, there is a good agreement (dashed line) with experimental data, if for  $J'$  the same value was assumed as for  $J$  ( $J/k_B \cong 7.5$  K).

The magnetic susceptibilities for tourmaline<sup>36)</sup> are anisotropic. The average susceptibilities  $\langle \chi \rangle = (\chi_{\parallel} + 2\chi_{\perp})/3$  were described by a Curie-Weiss law  $\langle \chi_g \rangle = C(T + \Theta)^{-1}$  with  $C = 4.29 \cdot 10^{-3}$  emu K/g and  $\Theta = 9$  K – Fig. 3b [71T2]. By using the amount of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  determined by chemical analysis, the spin only behaviour ( $S = 5/2$  and 2 for  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ ) leads to  $C = 4.15 \cdot 10^{-3}$  emu K/g, in agreement with experimental data. Taking into account the number of iron ions in Y and Z-sites and a random distribution of iron ions, and ignoring the Ti and Mn contributions the weighted average exchange interaction per magnetic ion is  $\langle J \rangle = 0.09 J + 0.35 J' + 0.18 J''$ . For a spin only behaviour  $\Theta = 2S(S+1) \langle J \rangle / k_B$ , where  $S = 5/2$  and 2 for  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  with average values  $S(S+1) = 7$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+} \cong 2$ . When using  $J/k_B = 7.5$  K a value  $(2J + J'')/k_B = 8$  K was obtained [71T2] from the average value  $J_{av}/k_B = 2$  K obtained for  $\Theta = 9$  K. Since of the longer distances between nearest neighbour YZ and ZZ pairs,  $J'/k_B$  and  $J''/k_B$  are expected to be smaller than  $J/k_B = 7.5$  K.

The anisotropy of the susceptibilities was attributed to crystal field effects on ferrous ions. The magnitude of the splitting of the lowest  $S = 2$  spin quintuplet is characterized by the parameter  $D_z$ . If we take this into account, the temperature dependences of the susceptibilities were given by [71T2].

$$\chi_{m\parallel}^{-1} = (k_B / 2Ng^2\mu_0\mu_B^2)(T - 2.1D_z / k_B) \quad (2)$$

$$\chi_{m\perp}^{-1} = (k_B / 2Ng^2\mu_0\mu_B^2)(T + 1.05D_z / k_B)$$

where, for a finite concentration of magnetic ions, it is necessary to replace  $T$  by  $T + \Theta$ . By solid lines in Fig. 3b the calculated values are plotted. For  $\mathbf{H} \parallel \mathbf{c}$ ,  $10^3 \chi_g^{-1} = (T + 22.6) / 4.286$  and for  $\mathbf{H} \perp \mathbf{c}$ ,  $10^3 \chi_g^{-1} = (T + 2.8) / 4.286$ . The agreement with experimental data is acceptable.

The tourmaline<sup>37)</sup> is magnetically isotropic – Fig. 3c [71T2]. As seen in Table 3, the ferrous to ferric atom ratio, as deduced from chemical analyses, is much smaller than for sample<sup>36)</sup>. In analyzing the data most  $\text{Fe}^{2+}$  ions were supposed to be at the Y-site, where the distortion from octahedral environment symmetry and hence  $D_z$  value is smaller than for the Z-site. Also, the major distortion of the oxygen octahedron about the Y-position is along the pseudo 4-fold axis O1 – O3 which makes approximately a  $65^\circ$  angle with the  $\mathbf{c}$ -axis in tourmaline structure and thus further reduces the anisotropy. Thus it was expected that  $\chi_{\parallel} = \chi_{\perp}$ . By fitting the experimental data, a dependence  $\chi_g^{-1} = (T + \Theta)/C$  with  $C = 6.26 \cdot 10^{-3}$  emu K/g and  $\Theta = 9.2$  K was obtained, whereas the spin only behaviour leads to  $C = 7.38 \cdot 10^{-3}$  emu K/g by using the results of chemical analysis. The spin only prediction is plotted as dashed line in Fig. 3c. Since there are two types of sites Y and Z, some deviations from a Curie-Weiss-type behaviour are expected. If the spins of ions located on Y- and Z-sites are denoted by  $S_1$  and  $S_2$ , and by using the molecular field approximation the following relation was obtained:

$$\langle S_i \rangle = [S(S+1)/3](g\mu_0\mu_B H / k_B T) + \sum_j [S(S+1)/3](2J_{ij} / k_B T) \langle S_j \rangle \quad (3)$$

for  $i = 1, 2$  and  $j = 1, 2$ .

The exchange constants,  $J_{ij}$ , are proportional to  $J$ ,  $J'$ ,  $J''$  except for a weighting factor. By solving the two equations (3) for  $i = 1$  or 2, the susceptibility was calculated, which is the weighted average  $\langle S_1 \rangle / H$  and  $\langle S_2 \rangle / H$ . Taking into account, as for tourmaline<sup>36)</sup>, that  $J/k_B = 7.5$  K and considering  $J'/k_B = 1$  K and  $J''/k_B = 6$  K, the calculated susceptibilities (solid line) describe rather good the experimental data. The experimental data show that, at 4.2 K, no magnetic order is evidenced in all the above studied tourmalines.

### 8.1.3.5.3 Neutron diffraction data

In [71T1] was reported that the neutron diffraction pattern of buergerite<sup>35)</sup> at 295 K and 4.2 K are essentially identical. No new peaks appear and there are no significant changes in the intensity of any peaks. It was concluded that there is no significant long range order down to 4.2 K.

### 8.1.3.5.4 Nuclear magnetic resonance (NMR) data

The satellite NMR resonance lines from  $^{11}\text{B}$ ,  $^7\text{Li}$ ,  $^1\text{H}$  and  $^{27}\text{Al}$  have been observed in several different **elbaite** crystals [73T1]. Compared to their central lines, the satellite lines were always weak, broad and hard to detect. The resonance spectra for  $\mathbf{B} \parallel \mathbf{c}$  are shown in Fig. 4; the  $-1/2 \leftrightarrow 1/2$  transition being the central line. The  $^{19}\text{F}$  signals have also been observed. They are much weaker than the proton signal indicating a high OH: F ratio. The analysis of the  $^{23}\text{Na}$  resonance spectrum shows that the upper limit for the quadrupole coupling constant is  $|e^2qQ/h| < 0.2$  MHz. The small quadrupole coupling constant implies that the nearest neighbour coordination symmetries about Na ions are not too different from cubic. The  $^7\text{Li}$  resonance was observed for  $\mathbf{B}$  in  $(ac)$  plane and for  $\mathbf{B} \perp \mathbf{a}$ -axis. Values  $|e^2qQ/h| = 0.16$  MHz and  $\eta = 0$  were obtained. For various orientations of  $\mathbf{B}$  with respect to the tourmaline crystal, a narrow and strong  $^1\text{H}$  resonance line was always observed. The narrow linewidths ( $< 4.10^{-4}$  T) indicate the absence of a nearby magnetic nucleus, and are consistent with the structural evidence of the presence of hydroxyl groups (the  $^{16}\text{O}$  nucleus is nonmagnetic with zero spin). Both Z(18c) and Y(9b) sites with distorted octahedral coordination are occupied by Al atoms. The  $^{27}\text{Al}$  satellites are broad and overlapping. Because of the absence of individual lines, it was only possible to derive an approximate value  $e^2qQ/h$  for  $^{27}\text{Al}$  in the more distorted Z(18c) sites. From the observed maximum inner satellite splitting of 0.16 T, a value  $|e^2qQ/h| \cong 6$  MHz was obtained [73T1].

Studies by  $^{11}\text{B}$  MAS NMR method were performed in order to analyze the site occupied by boron excess in tourmalines [61B1, 73T1, 86T1, 97E1, 97W1, 99T1, 00S1, 02M1, 02M2]. In few investigations of tourmaline group minerals evidence of tetrahedral boron was not detected [73T1, 86T1]. As example from  $^{11}\text{B}$  resonance in elbaite, values  $|e^2qQ/h| = 2.76(8)$  MHz and  $\eta \cong 0$ , for  $\mathbf{z} \parallel \mathbf{c}$ , were obtained. These data show that the nearest neighbour environments about boron atoms are almost axially symmetric, although the boron atoms are located at general positions in tourmaline-type structure [73T1]. In [97E1, 97W1] the presence of considerable amounts of B on the tetrahedral site of synthetic and natural excess boron tourmaline close to the idealized olenite end member was proved by  $^{11}\text{B}$  MAS NMR spectroscopy and single crystal structure analysis, respectively. In [99T1] several natural tourmalines were investigated having small amount of excess boron (3.04...3.37 B apfu). They proved by  $^{11}\text{B}$  MAS NMR spectroscopy the presence of the tetrahedral boron. The  $^{11}\text{B}$  MAS NMR spectra of **synthetic olenite** and **natural dravite** are shown in Fig. 5 [00S1]. Since  $^{11}\text{B}$  has a quadrupole nucleus ( $I = 3/2$ ), quadrupolar interactions contribute to the  $^{11}\text{B}$  MAS NMR spectrum, leading in general to a line broadening of the resonance signals. The degree of broadening depends on the  $^{11}\text{B}$  local symmetry. The spectrum of the dravite exhibits the typical broad and asymmetric signal (a double peak at 11.961 and 0.820 ppm) of the low symmetrical trigonal ( $\text{BO}_3$ ) group. Similar spectra were obtained previously [97W1, 99T1]. The spectrum of synthetic olenite<sup>29)</sup> shows, in addition to the broad asymmetric signal of the ( $\text{BO}_3$ ) group as in dravite (12.564 and  $\cong 2.50$  ppm), a second single sharp signal at  $-0.613$  ppm, typical for boron in the highly symmetric  $\text{BO}_4$  tetrahedron [00S1] – Table 6. This shows that boron occurs not only in trigonal coordination, but is also located in the tetrahedral ring site. In natural Al-rich, Fe-poor lithian tourmalines (elbaite), in addition to the main line, small additional peaks were found in some spectra at about 0 ppm which were interpreted as due to tetrahedral boron [99T1]. We note the remark of [00S1] that the replacement of Si by B at the T position of synthetic olenite has a considerable influence on the interactions of the OH groups with surrounding atoms. In [02M1] the  $^{11}\text{B}$  MAS NMR spectrum of natural olenite<sup>43)</sup> was analyzed. The simulated lineshape results from the superposition of two quadrupolar MAS lineshapes. The broad-lineshape with  $\delta_{\text{iso}} = 18.3$  ppm,  $\nu_Q = 1.41$  MHz and  $\eta = 0.11$  suggests the trigonal-planar environment of the  $\text{BO}_3$  group which exhibits a strong electric field gradient and a large quadrupole interaction. The narrow lorentzian lineshape is due to  $^{11}\text{B}$  situated in a coordination characteristic of tetrahedral  $\text{BO}_4$  group. Values  $\delta \cong -0.6$  ppm,  $\nu_Q = 0.3$  MHz and  $\eta = 0.00$  were obtained. The determined  $\text{BO}_3/\text{BO}_4$  ratio is 3.00/0.77 [02M1].

The  $^{29}\text{Si}$  MAS NMR spectrum of excess-boron olenite<sup>11)</sup> shows the presence of two lines [02M2]. The line at  $-88.7$  ppm was attributed to tetrahedrally coordinated silicon. The small sharp peak at  $-107.3$  ppm was attributed

to a quartz impurity. No signal of octahedrally coordinated silicon was visible. Consequently, octahedral Y and Z sites are exclusively occupied by  $\text{Al}^{3+}$  ions. The difference in charge which is generated by the partial replacement of  $\text{Si}^{4+}$  ions, by  $\text{B}^{3+}$  ions is compensated by protons leading to OH contents near 4.

The natural olenite<sup>43)</sup> was further studied by the  $^{29}\text{Si}$  MAS NMR method [02M1]. As above, the peak at  $\approx -90$  ppm reflects  $^{29}\text{Si}$  at the T site – Fig. 6. An additional shoulder at  $\approx -85$  ppm was observed. Since in this sample about 1 apfu of  $^{11}\text{B}$  in hexagonal ring is present, two  $^{29}\text{Si}$  signals are expected. The main signal is due to silicon connected (via oxygen bridges) to two other Si atoms in the hexagonal ring. The other signal (shoulder) was attributed to silicon connected to one Si and one B atom. As before, no signal corresponding to  $^{29}\text{Si}$  was observed. For silicates synthesized at high pressure (olenite) the presence of  $^{29}\text{Si}$  does seem so unlikely [00S1].

#### 8.1.3.5.5 Electron paramagnetic resonance (EPR) data

An isotropic EPR line with  $g = 4.302(6)$  was found in a natural single crystal of tourmaline. This line was ascribed to impurity  $\text{Fe}^{3+}$  occupying a host site with the axial field parameter  $D = 0$  and rhombic field parameter  $E \gg h\nu$  [72J1].

The EPR studies were also performed in order to analyse the defect centers in tourmalines. Three main color changes occur in tourmaline due to  $\gamma$ -irradiation: colorless to pink, pink to yellow and colorless to yellow [75N1]. The colors produced by irradiation in tourmalines are stable up to temperatures of about 250, 400 and 500...600°C, respectively. Metastable electron-hole trap centers were responsible for these types of colors centers [69B2, 90P1, 04K1]. From EPR, optical absorption and luminescence studies of pink elbaite, the color-causing center was associated with an absorption band at about 515 nm and was attributed to a hole center of type  $\text{Al}-\text{O}^-\text{Al}$  [69B2]. Together with atomic hydrogen produced through the irradiation process, it disappeared at about 400°C. In [90P1] three color-producing processes were mentioned in elbaite: (1)  $\text{O}^-$  centers, (2) Mn-related electron centers and (3) Mn intradefect absorptions. The  $\gamma$ -irradiation turns colorless elbaite yellow and generates two types of defects [02K1]. By using the EPR method, the defects were identified as an  $\text{O}^-$  hole trap center and an atomic hydrogen,  $\text{H}^0$ . It was speculated that the  $\text{O}^-$  center was responsible for the yellow color. In [04K1] a combination of EPR and ENDOR studies was used for the identification of the microscopic structure of the  $\text{O}^-$  hole trap center and optical detection of EPR (ODEPR) for a direct correlation of the EPR data of the radiation induced  $\text{O}^-$  center with the yellow color. According to [04K1], before irradiation, the EPR measurements on elbaite<sup>72)</sup> showed no paramagnetic defects. After irradiation, the Li-bearing elbaite<sup>73)</sup> turned yellow and two paramagnetic centers were observed. An  $\text{O}^-$  hole trap center is stabilized within the plane spanned by three Y sites, and is located in the structural channels formed by  $\text{Si}_6\text{O}_{18}$ . The  $g$  factor of this center is nearly axial with  $g_{\parallel} = 2.002(2) < g_e$  and  $g_{\perp} = 2.050(3) > g_e$ . The shifts from the free electron  $g_e$  value are similar to  $\text{O}^-$  in apatite which is typical for the impurity  $\text{O}^-$  in weak crystal field [79M1], with electron configuration  $1s^2 2s^2 2p^5$ . In case of the  $\text{O}^-$  center in tourmaline, the  $g$  tensor ( $\parallel a$  axis) is oriented along the channel ( $c$ -axis). The small anisotropy of the  $^{27}\text{Al}$  superhyperfine (shf) interaction (0.6(1) MHz) and the large negative  $^{27}\text{Al}$  isotropic shf interaction (−23.2(1) MHz) were analysed within the theory of exchange polarized transferred hyperfine interactions [85A1]. The  $\text{O}^-$  center was considered to be located at the O1 site on the threefold symmetry axis and relaxed into the plane where it has three nearest neighbours ( $2\text{Al}^{3+}, 1\text{Li}^+$ ) on the Y sites in that hexagonal plane. In this configuration there is no overlap between the  $\text{O}^-$  orbital with its axis parallel to the  $c$ -axis and the  $\text{Al}^{3+}$  core orbitals, and thus the origin of the shf interaction is the exchange polarization. During the irradiation process also atomic hydrogen,  $\text{H}^0$ , was created [04K1]. It is an electron-trap center and shows shf interaction with three nuclei with  $I = 1/2$ . The  $g$  factor of  $\text{H}^0$ ,  $g = 2.007(2)$ , is isotropic and shows a small positive shift ( $\delta g = 0.005$ ), typical for an s ground state of an  $\text{H}^0$  atom trapped in an ionic crystal [71S1]. The correlation of the yellow color with the  $\text{O}^-$  hole center, evidenced by ODEPR was also observed after annealing the samples. At  $T \approx 250^\circ\text{C}$ , not only the  $\text{O}^-$  hole trap and the  $\text{H}^0$  electron trap were destroyed, but the yellow color also disappears [04K1]. A plausible creation process for the two paramagnetic centers is that they are formed by destruction of hydroxyl ions in the O1 site ( $\text{OH}^- + \gamma \rightarrow \text{O}^- + \text{H}^+$ ). We note that in [69B1] was concluded that the pink color with an absorption band centered at 515 nm was related with an  $\text{O}^-$  center which showed thermal stability up to 400°C. In [04K1] was suggested that there was a superposition of at least two defect related absorption bands, a yellow and pink one. The yellow center was related with  $\text{O}^-$  and pink center may be due to Mn impurities.



#### 8.1.3.5.6 $^{57}\text{Fe}$ Nuclear gamma resonance (NGR) data

A large number of  $^{57}\text{Fe}$  NGR studies were performed on tourmalines [69D1, 72B1, 72B2, 73B1, 73H1, 74F1, 74P1, 75A1, 75B1, 76D1, 76S1, 78G1, 79K1, 79S1, 81B1, 84M1, 86K1, 88F1, 93F1, 94F1, 95F1, 96L1, 97P1, 98D1, 98F1, 99D1]. As mentioned in section 8.1.3.5.1, tourmalines accommodate  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in Y and Z octahedral sites. These two sites differ from each other in size and symmetry. The Y octahedron shares edges with two Y and two Z octahedra and is relatively larger than the smaller Z octahedron which shares three edges with two Z and one Y octahedra. Thus, the  $^{57}\text{Fe}$  NGR spectra of  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -bearing tourmalines, at first sight, might be expected to have a total of four possible doublets corresponding to  $\text{Fe}^{2+}(\text{Y})$ ,  $\text{Fe}^{2+}(\text{Z})$ ,  $\text{Fe}^{3+}(\text{Y})$  and  $\text{Fe}^{3+}(\text{Z})$  as identified by [72B2]. Another possibility is  $^{47}\text{Fe}^{2+}$ , presumably in low Si and Al samples. In addition, some tourmaline spectra are even more complicated because the edge sharing of octahedral sites promotes electron sharing. If the total Fe content of the tourmaline is high enough or ordered appropriately, Fe atoms in adjacent sites can share electrons, making possible the presence of electron charge delocalization doublets (ED) in the  $^{57}\text{Fe}$  NGR spectra. These represent the averaged valence states of the Fe atoms that are sharing electrons, a number somewhere between  $2+$  and  $3+$ . The ED doublets were reported in tourmaline spectra [74P1, 76D1, 79S1, 81B1]. In [88F1] was confirmed that the charge interactions were taking place between iron in adjacent Y and Z sites. In [97P1] was suggested that both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  occupy only the Y site in the structure and it was argued that previous assignment of Fe to the Z site just does not make sense crystallochemically. The multiple doublets, previously attributed to  $\text{Fe}^{2+}$ , were assigned to various combinations of nearest and next nearest neighbours. The variable compositions lead to different forms of  $^{57}\text{Fe}$  NGR spectra and complicate the analyses. Consequently, there are different points of view concerning the  $^{57}\text{Fe}$  NGR spectra analysis of tourmalines [98D1].

The  $^{57}\text{Fe}$  NGR spectra of tourmalines, at 4.2 K, show no magnetic hyperfine splitting [79S1]. This confirms that no magnetic order appears at this temperature, in agreement with magnetic and neutron diffraction data.

The  $^{57}\text{Fe}$  NGR studies were used to assign sites in tourmaline to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Early studies [73H1, 79S1, 84M1] assigned  $\text{Fe}^{2+}$  to the Y(9b) site and  $\text{Fe}^{3+}$  to the Z(18c) site. Later on, intervalence charge transfer (IVCT) between  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  were reported [81B1, 87M2, 87M3]. The existence of charge transfer phenomena has been also stressed by optical spectroscopy [74F1]. The data on site dimensions and ionic radii lead to the assignment of divalent and some trivalent Fe to the Y(9b) site with trivalent Fe substituting for Al in the Z(18c) site, but assignment of the doublet to  $\text{Fe}^{3+}$  in Z(18c) site was rare in  $^{57}\text{Fe}$  NGR spectroscopy on tourmaline [78G1, 79K1, 81B1, 84M1, 88F1, 95F1]. Some more recent data on natural tourmalines with known chemical composition have shown that  $\text{Fe}^{2+}$  can be present in the Z(18c) site [88F1, 89F2, 95F1]. Some samples showed  $\text{Fe}^{2+}$  in both the Y(9b) and Z(18c) site, whereas others have only  $\text{Fe}^{2+}$  in Z(18c) sites and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the Y(9b) site. Electron delocalization may take place between Y(9b) and the Z(18c) sites [95F1]. The isomer shifts and quadrupole splittings for natural tourmalines, reported by various authors, are shown in Fig. 7.

To understand the distribution of iron in tourmaline sites, samples with well defined compositions were synthesized at temperatures from 400 to 700°C, under a pressure of 100 MPa, by transformation of an  $\text{Fe}^{2+}$ -rich natural chlorite in the presence of  $\text{Na}_{0.5}\text{K}_{0.5}$ -feldspar, boric acid and  $\text{H}_2\text{O}$  in stoichiometric proportions [98F1]. The oxygen fugacity,  $f_{\text{O}_2}$ , of most experiments was buffered by solid assemblages including hematites, nickel-nickel oxide and quartz-fayalite-iron. It was possible to synthesize tourmalines with  $\text{Fe}^{2+}$  in the Z site and  $\text{Fe}^{2+}$  or  $\text{Fe}^{2+} + \text{Fe}^{3+}$  in the Y site. These site occupancies are similar to those observed in many natural samples – Fig. 7b.  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are located predominantly in the Y site in all synthesized tourmalines [98F1]. The doublets assigned to  $\text{Fe}^{2+}$  in the Y site show isomer shifts of  $\delta \approx 1.1$  mm/s and quadrupole splittings  $\Delta Q > 2.1$  mm/s – Fig. 7b. In many cases, particularly for tourmalines synthesized at relatively high  $T$ , fit of the spectra is better if two doublets are used for  $\text{Fe}^{2+}$  in the Y(9b) site, as already shown in natural tourmalines [79K1, 95F1]. In [79K1] the existence of three non-equivalent Y sites was suggested related to a local deformation of the coordination polyhedra due to distribution of cations having different ionic radii. According to [98F1] the distribution of divalent and trivalent Fe in the Y and Z sites as well as their ratio depends on the synthesis condition. For each  $f_{\text{O}_2}$  buffer, the  $^{57}\text{Fe}$  NGR data show that  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in the Y site was correlated positively with  $T$  and  $f_{\text{O}_2}$  for  $T < 550^\circ\text{C}$ . For higher temperatures, a negative correlation was observed. These relationships reflect the structural changes involving the localization of  $\text{Fe}^{2+}$  in the Z site and an increasing amount of Al in the Y site. The  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  can be represented by the general function  $(\% \text{Fe}^{3+}) = \exp(a \log f_{\text{O}_2} + b)$ . The curves

corresponding to each temperature are roughly parallel and equidistant. Some spectra and their analysis having a doublet that is characteristic to  $\text{Fe}^{2+}$  in the Z site were given in Table 7 and Fig. 7b [98F1].

In order to analyze the  $^{57}\text{Fe}$  NGR spectra of 47 natural tourmalines [98D1], both the [72B1] and [79K1, 97P1] interpretations were considered. In case of 39  $\text{Fe}^{2+}$  bearing samples, the two most prominent doublets correspond to  $\text{Fe}^{2+}$  with  $\delta = 1.09$  mm/s and  $\Delta Q \cong 2.47$  and 2.28 mm/s. The simplest models using either one  $\text{Fe}^{2+}$  doublet with a starting  $\Delta Q \cong 2.3$  mm/s or two doublets with  $\Delta Q = 2.47$  or 1.56 mm/s, as found by [72B1], give no convergent fit. In 7 samples the model with doublets at  $\cong 2.47$  and 1.56 mm/s was successful. In one spectrum only one  $\text{Fe}^{2+}$  doublet was found. This result is consistent with the remark that the larger  $\Delta Q(\text{Fe}^{2+})$  doublets are those with the sharpest, more intensive peaks [97P1].  $\text{Fe}^{3+}$  was found in 26 natural samples [98D1]. The two doublets with highest  $\Delta Q$  values ( $\cong 2.47$  and 2.28 mm/s) were assigned to Y sites (arbitrarily noted as Y1 and Y2) with different nearest-neighbour coordination. Since XRD studies suggest, in this case, that only Al and Mg occupy the Z site, with all iron in Y site, the lowest  $\text{Fe}^{2+}$   $\Delta Q$  doublet ( $\Delta Q \cong 1.60$  mm/s) was assigned to another Y site (Y3) with different next nearest neighbours from above. The interpretation of  $\text{Fe}^{3+}$  doublets raise some problems. In [72B2] the doublet with lower  $\Delta Q$  value ( $\Delta Q \cong 0.45$  mm/s) was interpreted to Y occupancy, and the higher one ( $\Delta Q \cong 0.8$  mm/s) to Z occupancy. This assignment has been followed by most subsequent workers in the field [97G2]. In this data set, the intensities of the  $\text{Fe}^{3+}$  doublets were generally much smaller than for the  $\text{Fe}^{2+}$  doublets, and as result their hyperfine parameters in unconstrained fits were highly variable. For this reason this assignment, only from  $^{57}\text{Fe}$  NGR data, is questionable. XRD refinements of tourmaline<sup>51)</sup> [69B1, 93G1] suggested the presence of some  $\text{Fe}^{3+}$  in Z site. The latter study found 20 % of the total Fe in Z and 80 % in Y-site. Neutron diffraction study [71T1] found 6.4 % of the atoms in Z to be of "M" type where M contains 95 % Fe. Thus, a  $^{57}\text{Fe}$  NGR spectrum with one large doublet corresponding to  $\text{Fe}^{3+}(\text{Y})$  and a small  $\text{Fe}^{3+}(\text{Z})$  doublet might be expected. Other XRD measurements performed on 11 tourmalines [98D1] do not find any Fe in the Z site. However, amounts less than about 0.20 cations per 31O formula unit probably would not show up. Therefore, it is difficult to obtain reliable data from XRD refinements on the  $\text{Fe}^{3+}$  occupancies.

Four typical spectra of tourmalines are shown in Fig. 8 [98D1]. Based on the above discussion in case of a buergerite<sup>51)</sup> which contains only  $\text{Fe}^{3+}$ , all the  $\text{Fe}^{3+}$  in Fig. 8a was assigned to  $\text{Fe}^{3+}(\text{Y})$ . For a sample which contains only  $\text{Fe}^{2+}$  – Fig. 8b – the  $\text{Fe}^{2+}$  was located in Y1, Y2 and Y3 sites. The spectrum of sample<sup>49)</sup> from Fig. 8c shows a small amount of the iron as  $^{4}\text{Fe}^{3+}$ , while  $\text{Fe}^{2+}$  is distributed among Y1, Y2 and Y3. The doublet with  $\Delta Q = 0.51(8)$  mm/s and  $\delta = 0.17(2)$  mm/s in sample<sup>49)</sup> was assigned to  $\text{Fe}^{3+}$  in tetrahedral coordination. In sample<sup>50)</sup> from Fig. 8d a peak due to electron delocalization is observed. Doublets representing delocalized electrons show hyperfine parameters which fall in between those assigned to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In [94F1] the ED doublets having  $\delta$  values 0.86, 0.84 and 0.71 mm/s were assigned to Y – Y, Y – Z and Z – Z shared electrons. In [98D1] the ED doublet with  $\delta = 0.82$  mm/s was interpreted as a delocalization of charge between adjacent Y and Z sites.

The  $^{57}\text{Fe}$  NGR spectra of irradiated tourmalines were studied [76D1]. A considerable broadening of the absorption lines was observed upon irradiation which was attributed to a transition through proton exchange and electron hopping between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  sites.

#### 8.1.3.5.7 Pyroelectric and piezoelectric properties

Tourmaline crystals are pyroelectric materials that develop an electrostatic charge when heated and cooled. The tourmaline pyroelectric coefficients  $p_3^\sigma$  range from  $\cong 1.8$  to 5.4  $\mu\text{C}/\text{m}^2\text{K}$ , at 296 K [15A1, 65G1, 65G2, 71F1, 75D1, 83G1, 89G1, 95H1]. The general form of the pyroelectric response with temperature is plotted in Fig. 9 [95H1]. A polarity inversion of  $p_3^\sigma$  in tourmaline was obtained at  $T < 20$  K [75D1, 89G1]. The high-temperature region of the curve adopts one of two forms evidenced in Fig. 9. First, there is an upward inflection of the curve. This behaviour has been noted – Fig. 9 – for a pale rose sample above 450 K [83G1, 89G1], for a dark-green sample above  $\cong 420$  K and for a black sample above  $\cong 400$  K [99H1]. A similar inflection is predicted for the thermal expansion versus temperature in some minerals [95H1]. Thermal expansion causes the secondary pyroelectric effect which is a strong effect in tourmaline. Thus, this region of the curve reflects the effects of anharmonic vibration on pyroelectricity. Second, a smooth decrease in the pyroelectric coefficient was observed. For example, this trend was reported by [95H1] above 430 K for a schörl<sup>52)</sup> sample. This behaviour was assigned to the onset of electrical conductivity.

The amount of Fe in tourmaline has a prominent influence on the pyroelectricity. The increase of the iron content linearly decreases the pyroelectric coefficient for the composition range between 0.01(1) and 14.6(2) wt % FeO [95H1]. Thus, to a first approximation, tourmaline pyroelectric coefficients may be predicted directly from chemical composition. This effect could be caused by an increase in electrical conduction of Fe-rich tourmaline at elevated temperatures.

The relationship between pyroelectricity and composition indicates that the pyroelectric coefficient is influenced to different extents by the occupancies of the X, Y and Z cation sites [95H1]. The octahedral Y site occupancy strongly influences the pyroelectric coefficient due to preference of Fe for this site. The addition of Fe and Mg cations to the smaller Z octahedral site causes the pyroelectric coefficient to increase. However, because an extended suite of samples was not available in which the Z site contains ions other than Al, this proposed trend has not been experimentally determined [95H1]. The chemistry of the ninefold coordinated X site and the population of this site do not influence the pyroelectric coefficients of tourmaline.

Measurements and calculations have shown tourmaline  $\text{NaMg}_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH})_4$  to be a useful surface-acoustic-wave delay medium [72L1]. In particular, its combination of high velocity and very low propagation losses, together with a moderate piezoelectric coupling strength, makes it suitable for use at high frequencies. The velocity is typical  $4.4 \cdot 10^3$  m/s and occasionally rise to  $\approx 5 \cdot 10^3$  m/s when it merges with the slow shear bulk wave. The effective piezoelectric coupling constant  $k_{\text{eff}}^2$  with crystal plane Z and direction of propagation X or Y is 0.28(2) %. For crystal plane X and Y and direction of propagation Z,  $k_{\text{eff}}^2 < 0.02$  %. The temperature dependence of the delay time on the basal plane is 44(5) ppm/°C [72L1], in broad agreement with values for bulk waves in tourmaline [50M1].

#### 8.1.3.5.8 Electron energy loss spectroscopy (EELS)

The EELS study on synthetic olenite<sup>29)</sup> and natural dravite are shown in Fig. 10 [00S1]. In case of the synthetic olenite crystal, the presence of tetrahedral boron can be observed. For threefold-coordinated boron, in the natural dravite, the B K energy-loss near edge structure is dominated by a sharp peak at 193.3 eV, because of transitions to unoccupied states of  $\pi^*$  character due to the presence of  $\text{sp}^2$  bonding within the structure, followed by a broader peak at 202.3 eV attributed to states of  $\sigma^*$  character [95G1]. For fourfold-coordinated boron, the B K ELNES consists of a sharp rise in intensity with a maximum at about 198 eV followed by several weaker structures which were interpreted as transitions to states of antibonding  $\sigma^*$  character due to the  $\text{sp}^3$  bonding within the  $(\text{BO}_4)$  units [95G1]. The EELS spectrum of synthetic olenite exhibits all the peaks outlined, thus providing boron to occur both in trigonal and tetrahedral coordination. The molar proportion of boron in the two coordinations is  $f = {}^{[3]}\text{B}/({}^{[3]}\text{B} + {}^{[4]}\text{B}) = 0.758(152)$  [00S1].

#### 8.1.3.5.9 Optical properties

##### Raman spectroscopy

There are only few studies on tourmalines based on Raman spectroscopy. The reason is the complicated structure which requires sophisticated identification of spectral peaks. In [69G1] Raman shifts in tourmalines were systematized in terms of the vibrational modes of rings of  $\text{SiO}_4$  tetrahedra. In [78A1] Raman spectra of four single crystals of tourmaline were presented in the frequency range  $100 \dots 1200 \text{ cm}^{-1}$ , suggesting that the  $\text{Si}_6\text{O}_{18}$  rings can hardly be considered as separate vibrational units. On the contrary, [89P1] reported polarized Raman spectra of natural tourmalines in which the major peaks in the spectral range below  $1200 \text{ cm}^{-1}$  were related to modes of hexagonal  $[\text{Si}_6\text{O}_{18}]^{12-}$  rings. In [97G1] the tourmalines were studied by Raman spectroscopy in the frequency range  $150 \dots 1550 \text{ cm}^{-1}$  where cation – oxygen vibrational modes are Raman active. For calculations, the  $\text{Si}_6\text{O}_{18}$  ring was considered as a separate unit whose internal vibrational modes are sensitive to the neighbouring cations of the ring (i.e. X-, Y- and Z- positioned cations). Boron-oxygen and aluminium-oxygen vibrations should be treated as modes of a combined B–Al–O network and, as a result, the modes which include symmetric B–O stretching give rise to peaks at about  $750 \text{ cm}^{-1}$ . The peak at  $1400 \text{ cm}^{-1}$  arises from anti-symmetric B–O stretching vibrations [97G1]. On this basis criteria for classifying these minerals were proposed. The polarized Raman spectra for elbaite are shown in Fig. 11. The type of vibrations was determined on the basis of calculated spectra of small clusters with imposed boundary conditions [96M1]. The factor group analysis of

tourmalines predicts 28  $A_1$  and 49  $E$  Raman active modes, but it was shown that it is impossible to observe them all experimentally. The character table of the tourmaline point group determines the kind of phonons (transverse (T) or longitudinal (L)) as expected in different geometries. The Raman spectra differ according to composition. Most marked differences, as a result of various compositions, are observed in the low-frequency band (LFB) at about  $230\text{ cm}^{-1}$  and for the mid-frequency band (MFB) at about  $670\text{ cm}^{-1}$ . The latter arises from  $\text{Si}_6\text{O}_{18}$  ring vibrational modes, localized in the bridging oxygen atoms, whose frequencies are strongly influenced by the Y-cations, while the band at  $230\text{ cm}^{-1}$  is directly controlled by Y–O bond stretching. The band at  $370\text{ cm}^{-1}$  arises from Al–O bond stretching modes, the  $670\text{ cm}^{-1}$  from symmetrical Si–O–Si vibrations and the  $1020\text{ cm}^{-1}$  band from Si–O band stretching. By using these two bands, the type of predominant cations in Y-positions was estimated [97G1]:

- tourmalines of the buergerite – schörl type in which more than a half of the Y-positions are occupied by Fe. Their spectra are characterized by a single peak at  $238(2)\text{ cm}^{-1}$  in the LFB and three resolved peaks at  $635(3)$ ,  $674(3)$  and  $697(3)\text{ cm}^{-1}$  in the MFB;

- tourmalines of the elbaite type, characterized by a sharp peak at  $224(2)\text{ cm}^{-1}$  in the LFB and two well-separated peaks in the MFB with frequencies at  $638(3)\text{ cm}^{-1}$  (asymmetric) and higher than  $707\text{ cm}^{-1}$  (sharp symmetric) – Fig. 11;

- tourmalines close to the dravite type, in which more than a half of the Y-positions are occupied by Mg. Their spectra are characterized by two peaks, in the LFB at  $215(3)$  and  $237(3)\text{ cm}^{-1}$ , while one peak at  $698(4)\text{ cm}^{-1}$  can be resolved in the MFB. The type of Y-positioned cations also influences the O–H stretching modes which generate peaks with frequencies above  $3000\text{ cm}^{-1}$ .

### Infrared spectra

IR studies were also performed on tourmalines [79R1, 88G2, 96R1, 00S1]. These studies have in view mainly the OH-stretching region. For example, in [88G2] the influence of composition on the spectra was analysed in order to differentiate the bands associated with the two types of OH and to assign the observed IR components to the different chemical environments of OH groups. The hydroxyl stretching region of the IR spectrum of different tourmalines are shown in Fig. 12 [88G2]. Absorption maxima and assignment associated with various environments of the observed IR stretching bands are given in Table 8. The hydroxyl stretching region depends mainly on the composition of the octahedral Y-sites. The correlation between chemical composition and the IR spectra has permitted the assignment of the more intense components to OH located at the border of brucite fragments and coordinated to  $\text{AlAlLi}$ ,  $\text{AlAlM}^{2+}$  ( $\text{M}^{2+} = \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}$ ) and  $\text{AlAlAl}$  associations. The  $\text{AlAlFe}^{2+}$  association has been confirmed by the thermal dehydroxylation of Fe-elbaite. The OH coordinated to  $\text{Fe}^{2+}$  is lost at lower temperatures than the other ones. The occupancy of X sites by  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  or vacancies shifts the IR components towards lower frequencies as a consequence of the lower electrostatic repulsion between the proton and X cations. The simultaneous occupancy of X-sites by different cations is the origin of the experimental broadening observed in these components. The analysis of highest frequency bands of the stretching region ( $3750\ldots 3600\text{ cm}^{-1}$ ) has permitted the assignment of the observed components to the OH located at the centre of hexagonal rings and coordinated to  $\text{M}^{2+}\text{M}^{2+}\text{M}^{2+}$  (dravite and schörl),  $\text{AlAlLi}$  (elbaite) and  $\text{AlM}^{2+}\text{Li}$  (Fe, Mn-elbaite). The correlation between the OH orientation, as deduced from the IR study of single crystals and the chemical composition, has shown that only in the case of OH, coordinated to three divalent Y-cations, the bond is nearly parallel to the  $c$ -axis of tourmaline. When the three cations have not the same charge or the OH groups can be involved in hydrogen bonds with other structural oxygens (OH located at the border of hexagonal rings) the orientation of OH bonds deviate considerably from the trigonal  $c$ -axis direction.

The above study was continued by [96R1] who analyzed the dravite in which OH was partially substituted by F. As above mentioned [88G2], the high-wave number bands ( $> 3600\text{ cm}^{-1}$ ) are particularly sensitive to the X-site occupancy and to the cation distribution over the adjacent Y sites ( $\text{M}^{2+}$ ,  $\text{M}^{3+}$ ). The lower wave number bands ( $3300 < \nu_{\text{OH}} < 3600\text{ cm}^{-1}$ ) reveal the cationic distribution over the Y and Z sites. The valence state of the Y-cations can be characterized from  $\nu_{\text{OH}}$  wavenumbers of both inner and outer hydroxyl groups. The OH  $\rightarrow$  F substitution is restricted to the inner hydroxyl groups as for example in dravite – Fig. 13 [96R1]. It is impossible if the X-site is vacant as for example in Mg-foitite. In the  $1400\ldots 1300\text{ cm}^{-1}$  wave number range, antisymmetric vibrations of the  $\text{BO}_3$  group were observed. From bond valence considerations, it was possible to identify the nearest cationic neighbours of the three oxygens of the coordination triangle of boron. A band at  $\approx 1380\text{ cm}^{-1}$  indicates the presence of  $2\text{Mg}^{2+}$  at the two Y sites adjacent the O2, also bonded to  $\text{B}^{3+}$ , whereas a band at  $\approx 1340\text{ cm}^{-1}$  is typical of the presence of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  at these two Y sites. A low-wave number band, typically around

1290  $\text{cm}^{-1}$  can be assigned to oxygen O8, bonded to  $\text{B}^{3+}$  and to  $2\text{Al}^{3+}$  at the two adjacent Z sites. The Si–O stretching regions in the 1200...800  $\text{cm}^{-1}$  range are complicated owing to the strong anisotropy of tetrahedra. However, it is easy to distinguish the short Si–O $\perp$  bond (perpendicular to the ring of tetrahedra) which is shorter than other Si–O bonds and generates a high-wave number band, around 1100  $\text{cm}^{-1}$ . All these band wavenumbers are sensitive to the X, Y and Z site occupancies. In particular, the anisotropy of  $\text{SiO}_4$  tetrahedron, revealed by the split Si–O stretching bands, strongly depends on the X-site occupancy. In the range 800...350  $\text{cm}^{-1}$  many vibration modes, are observed:  $\partial\text{BO}_3$ , between 800 and 600  $\text{cm}^{-1}$ , symmetric Si–O–Si band at  $\approx 700 \text{ cm}^{-1}$ ,  $\nu_{\text{Mg-O}}$ ,  $\nu_{\text{Al-O}}$  and  $\partial_{\text{Si-O}}$  below 600  $\text{cm}^{-1}$  and several  $\partial_{\text{OH}}$  [96R1].

The FTIR spectrum of synthetic olenite<sup>29)</sup> and their interpretation is shown in Fig. 14 [00S1]. The characteristic bands for both the inner and outer hydroxyl groups in tourmaline structure, as previously reported [88G2], are present, thus suggesting a more or less “normal” OH-content (near 4.0 apfu) of the synthetic olenite. The wave number for the inner OH-group (OH1), 3597  $\text{cm}^{-1}$ , has the lowest value measured in tourmalines, but falls into the range generally valid for the outer OH-groups [88G2]. For the outer OH-groups (OH3) of synthetic olenite, two strong bands are present. The band at 3367  $\text{cm}^{-1}$  has the lowest known wave number for any tourmaline. The two extreme band positions were attributed to the fact that the hydroxyl protons interact by hydrogen bonding with underbonded oxygens of the ring tetrahedra, thus providing indirect evidence for the presence of  $\text{BO}_4$  tetrahedra in the  $\text{T}_6\text{O}_{18}$  ring unit. Note that for normal hydroxyl-tourmalines without tetrahedral boron, there is almost no hydrogen bonding between the O1 site and surrounding oxygens [93R2]. The stretching band at 3493  $\text{cm}^{-1}$  has a normal wave number and is caused by hydrogen bonding with oxygen shared by adjacent  $\text{SiO}_4$  tetrahedra of the ring.

The IR spectrum of excess-boron olenite<sup>43)</sup> shows a main signal at  $\approx 3460 \text{ cm}^{-1}$  and a weak signal at  $\approx 3590 \text{ cm}^{-1}$  which were assigned to the OH3 groups. The weak band at  $\approx 3650 \text{ cm}^{-1}$  may represent the contribution from the OH1 group [02M1]. As an example of tourmaline without  $^{14}\text{B}$ , there is the IR spectrum of dravite which shows OH-stretching bands at  $\approx 3740 \text{ cm}^{-1}$  (OH1) and at  $\approx 3570 \text{ cm}^{-1}$  (OH3). These values are lower than those reported for a synthetic excess-boron olenite [00S1]. The natural olenite containing  $\approx 1$  apfu B at the T site shows intermediate values. As mentioned above, the shifts of the band compared to dravite give indirect indication for the presence of  $\text{BO}_4$  tetrahedra in the hexagonal ring. The tetrahedrally coordinated B introduces a charge deficit into hexagonal ring, by replacement of  $\text{Si}^{4+}$  by  $\text{B}^{3+}$ . Underbonded O atoms of the ring form relatively strong hydrogen bands with the protons of the hydroxyl groups. This leads to a shift of OH stretching bands [02M1].

### Absorption spectra

The interpretation of absorption bands in the optical spectra of natural Fe-bearing tourmalines was a matter of debate [93T1]. Most samples are characterized by two broad intense absorption bands at  $\approx 9000$  and  $\approx 14000 \text{ cm}^{-1}$  (usually  $\sigma \gg \pi$ ) – Fig. 15. These were assigned [68F1, 69M1, 69W1, 70T1] to components of the  $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$  transition in the  $\text{Fe}^{2+}$  ions on the Y-sites. On the other hand in [72B2, 88C1] was believed that these bands are a superposition of two pairs of closely located bands caused by  $\text{Fe}^{2+}$  ions in Y- and Z-sites. Due to the strong polarization ( $\sigma \gg \pi$ ) and because of the temperature dependence of band intensities in  $\sigma$ -polarization, [78S1, 87M3] attributed the  $\pi$ -polarized  $\approx 9000$  and  $\approx 14000 \text{ cm}^{-1}$  bands to spin allowed d-d transition in  $\text{Fe}^{2+}(\text{Y})$  and  $\text{Fe}^{2+}(\text{Z})$ , and those in  $\sigma$ -polarization to d-d transitions enhanced in intensity by exchange interaction with neighbouring  $\text{Fe}^{3+}$  ions. In [84M1] features were suggested caused by electron transitions in exchange coupled  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$  pairs in Y–Y and Z–Z sites of the structure of some  $\text{Fe}^{3+}$ - and  $\text{Fe}^{3+}, \text{Fe}^{2+}$ - tourmalines.

The optical absorption spectra of tourmaline solid solutions containing Fe, Fe+Ti, Cr, Ni, Cu, Co, Mn chromophoric centers, grown hydrothermally at 650 °C and 1.5 kbar were studied [90T1, 93T1]. Typical spectra of samples with high-doping level are shown in Fig. 15a. Two broad intensive absorption bands a and b are, in polarization, shape and position, close to the bands in spectra of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ -bearing natural tourmalines with high iron content. Like in natural tourmalines, bands c and d in  $\pi$ -polarization which are always much less intensive than bands a and b, have nearly the same energies as the latter. The band e was connected with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  chromophoric ions too and occurs as a shoulder at the high-energy wing of band a. In the spectra of Fe–Ti tourmaline besides the  $\sigma$ -polarized bands similar to bands a and b, the high-energy part shows additional bands i and j, having strict  $\sigma$ -polarization (Fig. 15b). In polarized spectra of  $\text{Mn}^{3+}$ , Li free sample, four intensive absorption bands (a, b, c, d) can be observed (Fig. 15c). In  $\text{Mn}^{3+}$ -bearing tourmaline with Li admixture were shown bands e, g, h in  $\sigma$ -polarization and one (f) in  $\pi$ -polarization (Fig. 15d). The entering of Li in Y sites leads

to a significant change of the shape of absorption curves. The origins of the transitions are given in Table 9 [93T1]. It was concluded that for most of the synthetic  $\text{Fe}^{2+}\text{-Fe}^{3+}$ -bearing samples the presence of intensive  $\sigma$ -polarized absorption bands is characteristic. These bands are caused by exchange coupled  $\text{Fe}^{2+}\text{-Fe}^{3+}$  pairs in Y–Y and Y–Z sites. An additional intensive absorption band at  $12500\text{ cm}^{-1}$  ( $\sigma$ -polarization) appears in some samples but not in natural tourmalines. The color and spectroscopic properties of the  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{Cu}^{2+}$  containing tourmalines are significantly affected by the presence of small Li-content. The data suggest that  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  ions occupy predominantly the Y site of tourmaline structure, whereas the  $\text{Cu}^{3+}$ -ions seem to enter the smaller Z-octahedra. The optical spectra of  $\text{Cu}^{2+}$ -[90F1, 93T1], Cr-[69M1, 80S3, 88B1, 89S1, 93T1], Co-[93T1] and Ni-[76P1, 93T1] bearing tourmalines were also studied. For a review see [93T1].

The optical absorption spectra of tourmalines were also analyzed as function of pressure – Fig. 16 [96T1]. The spectrum of Fe,Ti rich schörl<sup>[68]</sup>, at ambient pressure, characteristically displays two absorption bands, as discussed above, near  $13700\text{ cm}^{-1}$  (a) and  $9090\text{ cm}^{-1}$  (b) typical of Fe-bearing tourmalines. On increasing pressure, bands a and b gain intensity and energy which amounts in the latter case to  $125\text{ cm}^{-1}/\text{GPa}$  for a and  $160\text{ cm}^{-1}/\text{GPa}$  for b. In addition to bands a and b, a broad envelope occurs in the  $17000\text{...}25000\text{ cm}^{-1}$  range with two weak component bands near  $18800\text{ cm}^{-1}$  and  $20600\text{ cm}^{-1}$ , respectively at ambient pressure. These bands exhibit different response to pressure in their position and intensity:  $210\text{ cm}^{-1}/\text{GPa}$  for that from  $18800\text{ cm}^{-1}$  and  $300\text{ cm}^{-1}/\text{GPa}$  for  $20600\text{ cm}^{-1}$  band. All these changes cause intensification of the color of the sample from light greenish-gray, at atmospheric pressure, to dark green at higher pressures. The bands a and b, caused by  $\text{Fe}^{2+}$  dd-transitions in elbaite and schörl, for  $\mathbf{E}$  parallel to possible  $\text{Fe}^{2+}\text{-Fe}^{3+}$  pairs, show a pressure and temperature behaviour of their intensity different to that of ordinary dd-transitions of isolated  $\text{Fe}^{2+}$ . These were interpreted by exchange coupling effects; ECP in  $\text{Fe}^{2+}\text{-Fe}^{3+}$  pairs. The intensities of these bands decrease on heating. At higher temperatures ( $T \geq 700\text{ K}$ ) their integral intensities remain constant. Thus, when decreasing the temperature only the portion of intensities of the ECP-bands a and b gained from exchange interaction between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions changes and does not influence that part of the intensity which is produced by the ordinary dd-transitions in “isolated”  $\text{Fe}^{2+}$  ions. In the spectral range of  $17000$  to  $26000\text{ cm}^{-1}$ , the band system gains intensity with pressure. Two explanations were suggested [96T1]: (1) traces of  $\text{Ti}^{3+}$  exchange coupled to  $\text{Fe}^{2+}$  show the above pressure effect typical of exchange coupled pair; (2) there occurs a pressure-induced increase of the number of  $\text{Ti}^{3+}$  ions of the expense of  $\text{Ti}^{4+}$  in Y-positions, induced by  $\text{Fe}^{2+}$  in connected Y-octahedra, whereby OH in trans-configuration of Y-octahedra promote this process.

Other optical studies were performed on tourmalines. The intense color of green, blue and black tourmalines have been ascribed to optically induced charge transfer between adjacent cations. However, the optical spectroscopy of iron bearing tourmalines is not typical of mixed valence systems. We mentioned already that in [78S1, 78S2, 80S1] as effect of interaction between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , the intensification of the characteristic absorption of  $\text{Fe}^{2+}$  was proposed. In [87M3] was reported a study of  $\text{Fe}^{2+}\text{-Fe}^{3+}$  interactions in tourmaline which directed toward a quantitative characterization of intensified  $\text{Fe}^{2+}$  transitions. The basic characteristics of  $\text{Fe}^{2+}$  absorption as function of iron content, in tourmaline, are illustrated in Fig. 17 [87M3]. At very low iron contents and low  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios, as in tourmaline<sup>[69]</sup>, the spectroscopy of non-interacting  $\text{Fe}^{2+}$  can be seen – Fig. 17a. The broad bands centered at  $720\text{ nm}$  and  $1250\text{ nm}$ , as above discussed, were assigned to components of  $^5\text{T}_2 \rightarrow ^5\text{E}$   $\text{Fe}^{2+}$  transition split by the noncubic crystal field [78S1]. The intensity of these transitions in  $\mathbf{E} \perp \mathbf{c}$  does not exceed that in  $\mathbf{E} \parallel \mathbf{c}$ . The sharp bands between  $1300$  and  $1500\text{ nm}$  are vibrational transitions.

A comparison of this spectrum to that of typical tourmaline<sup>[70]</sup> – Fig. 17b – shows the basic features of  $\text{Fe}^{2+}\text{-Fe}^{3+}$  interactions. Absorption intensity in  $\mathbf{E} \parallel \mathbf{c}$  has increased linearly with Fe content. This behaviour is typical of transition elements in most environments. The same transitions in  $\mathbf{E} \perp \mathbf{c}$  have increased  $\sim 10$  times over the increase in Fe content. The added intensity in  $\mathbf{E} \perp \mathbf{c}$  can be attributed to  $\text{Fe}^{3+}$  as demonstrated by partial oxidation of natural samples [69W1, 78S1]. The difference in intensity is related to the intensification of  $\text{Fe}^{2+}$  absorption by adjacent  $\text{Fe}^{3+}$ . Extrapolations indicate that pairs of  $\text{Fe}^{2+}\text{-Fe}^{3+}$  have  $\text{Fe}^{2+}$  absorption intensity  $\sim 200$  times as great as isolated  $\text{Fe}^{2+}$ . Enhanced  $\text{Fe}^{2+}$  absorption bands are recognized in tourmaline by their increase at  $78\text{ K}$ , up to  $50\%$ . Enhancement of  $\text{Fe}^{2+}$  absorption intensity provides a severe limitation on the accuracy of determinations of  $\text{Fe}^{2+}$  concentration and site occupancy by optical spectroscopy methods.

The origins of color and pleochroism of tourmalines were studied. In the green and blue tourmaline [68F1], an absorption band in the red end of the spectrum was shown, the band having maximum intensity when the vibration direction of the electric field of incident light lies in the 001 plane (i.e.  $\mathbf{E} \parallel (001)$ ). The pleochroic band was assigned to  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge transfer in the (001) plane. The color and pleochroism of brown tourmalines

were attributed to  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  interaction in the 001 plane [68M1], the band in the blue region at  $22000\text{ cm}^{-1}$  having maximum intensity in  $E \parallel (001)$  spectra. The color and pleochroism of pink tourmalines were attributed to  $\text{Mn}^{3+}$  [68M1]. In [68R1] the pleochroic  $13800\text{ cm}^{-1}$  band in green and blue tourmalines was assigned to  $\text{Fe}^{2+} - \text{Fe}^{3+}$  charge transfer. In [69W1] the  $13800\text{ cm}^{-1}$  band was attributed to  $\text{Fe}^{2+}$  in distorted sites of  $D_{4h}$  symmetry. The spectra of Cr-bearing tourmaline [87M1] exhibit two strong absorption bands at  $17000\text{ cm}^{-1}$  and  $24000\text{ cm}^{-1}$ . These mark the transitions  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  in octahedrally-bonded  $\text{Cr}^{3+}$ . The natural silicate is green in the  $E \parallel (001)$  orientation and yellow-green in the  $E \perp (001)$  orientation. The absorption bands at  $9000\text{ cm}^{-1}$  in black tourmalines were attributed to  ${}^5\text{T}_2 \rightarrow {}^5\text{E}(\text{D})$  transition in octahedrally bonded  $\text{Fe}^{2+}$  [69W1, 87M1]. This band is slightly pleochroic in terms of intensity but not energy, with a maximum intensity in  $E \parallel (001)$  spectra. The absorption band at  $13800\text{ cm}^{-1}$  is markedly pleochroic with minimum intensity in  $E \perp (001)$ . The  $23500\text{ cm}^{-1}$  band in black tourmalines marks the field-independent transitions  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 {}^4\text{E}(\text{G})$  in  $\text{Fe}^{3+}$ . In one natural tourmaline (Villeneuve) which contains more Mn, and because  $\text{Mn}^{2+}$  adsorbs weakly at  $24500\text{ cm}^{-1}$  and  $23000\text{ cm}^{-1}$  [68M1], the broadness of the  $23500\text{ cm}^{-1}$  band was attributed to  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 {}^4\text{E}(\text{G})$  and  ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 {}^4\text{T}_2(\text{G})$  transitions in Mn [87M1]. Buergerite shows absorptions in the near infra-red and red regions, but most features in the visible are swamped by charge transfer bands [87M1].

The effects of  $\gamma$ -irradiation on the color of tourmalines were also analysed. In [75N1] color changes were observed on  $\gamma$ -irradiation over 500 colorless, pink, blue and green tourmalines. Significant changes were the development or intensification of pink or the development of yellow superimposed on the preexisting color. Irradiation and heating indicates the possibility of at least seven causes of pink and two causes of yellow colors in tourmalines. Some of these colors are stable to heat, and some not. This complexity may explain the diversity of the assignment for the origin of the pink color. As mentioned already, three main color changes occur in tourmaline due to  $\gamma$ -irradiation: colorless to pink, pink to yellow and colorless to yellow. Metastable electron-hole centers were responsible for these types of color centers [90P1] – see section 8.1.3.5.5. In [88R1] was suggested that irradiation-induced color in Li-bearing tourmaline is due to oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ . By using the intensity ratio of the bands of  $\text{Mn}^{2+}$  at  $414\text{ nm}$  ( $\approx 24150\text{ cm}^{-1}$ ) and  $\text{Mn}^{3+}$  at  $515\text{ nm}$  ( $\approx 19400\text{ cm}^{-1}$ ) it was concluded that for a selected sample exposed to a controlled dose of  $\gamma$ -rays, 24.3 % of  $\text{Mn}^{2+}$  was oxidized to  $\text{Mn}^{3+}$ . In [88D2] optical absorption spectra ( $4000\text{--}30000\text{ cm}^{-1}$ ) of natural and  $\gamma$ -irradiated pink and green tourmalines were studied. A sharp band at  $7000\text{ cm}^{-1}$  was observed. It was ascribed to vibrations of  $\text{H}_2\text{O}$ . Bands at  $8500\text{ cm}^{-1}$  and  $14800\text{ cm}^{-1}$  were assigned to d-d transitions of  $\text{Fe}^{2+}$  at distorted octahedra of  $\text{MO}_4(\text{OH}, \text{F})$  and  $\text{M}'\text{O}_5(\text{OH})$  respectively, where  $\text{M} = \text{Li}, \text{Al}$  and  $\text{M}' = \text{Al}$ . The bands at  $7000\text{ cm}^{-1}$  and  $8500\text{ cm}^{-1}$  were not considered by [88R1]. The additional bands around  $19500\text{ cm}^{-1}$  and  $25500\text{ cm}^{-1}$  [88R1], were assigned by [88D2] to  $5\text{E} \rightarrow 5\text{A}_1$  and  $5\text{B}_2 \rightarrow 5\text{A}_1$  d-d transitions of  $\text{Mn}^{3+}$  in  $\text{M}'\text{O}_5(\text{OH})$  sites, respectively. The pink color increases in intensity by  $\gamma$ -irradiation and adopt a yellow tint, mixed with the original pink [88D2]. Heating at  $500^\circ\text{C}$  eliminated the pink color but the yellow was not affected. Above  $600^\circ\text{C}$  the crystal becomes colorless. Green tourmaline become pink after irradiation [90P1]. The increase of  $\gamma$ -ray doses yielded two steps in the growth of absorption intensity of absorbances measured for  $k \parallel c$  ( $19500\text{ cm}^{-1}$ ) and  $k \perp c$  ( $25500\text{ cm}^{-1}$ ). These results were interpreted in terms of at least two different centers. The bands at  $8500$  and  $14800\text{ cm}^{-1}$  became more intense with increasing dose of irradiation [88D2]. It is not clear whether this is due to a reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ .

Two possible mechanisms for producing the color of Mn doped samples were considered: (1) oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  [88R1] and a reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  [88D2]. The EPR results did not reveal the presence of  $\text{Mn}^{2+}$  ions. Thus, in [88D2] was suggested that irradiation will produce conduction and valence holes that can be trapped by  $\text{Mn}^{4+}$  in  $\text{M}'\text{O}_5(\text{OH})$  sites, yielding an electron trap for  $\text{Mn}^{4+}$  and a hole trap for  $\text{Li}^+$ . Thus, the precursor center for the color-producing  $19500\text{ cm}^{-1}$  band was assigned to  $\text{Mn}^{4+}$  in the  $\text{M}'\text{O}_5(\text{OH})$  sites.

In [69B2] studied irradiated elbaite crystals by EPR, optical absorption and luminescence. The EPR pattern, the broad optical absorption band at  $515\text{ nm}$ , the broad luminescence band at  $570\text{ nm}$  and the coloring of crystals, decreased gradually after heating up to  $500^\circ\text{C}$ , where they disappeared [69B2]. As mentioned in section 8.1.3.5.5, the pink color with an absorption band centered at  $515\text{ nm}$  was related initially with an  $\text{O}^-$  center which showed thermal stability up to  $400^\circ\text{C}$  [69B2]. According to [04K1] there is a superposition of at least two defect-related absorption bands, a yellow and a pink one. It was concluded that the yellow center was related with  $\text{O}^-$  defect and the pink center may be due to Mn impurities.

For optical spectra of Mn-rich elbaite (tsilaisite) see [86S2].

The refractive indices of some tourmalines are listed in Table 10.