THE STRUCTURE OF TOURMALINE

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ABSTRACT

The structure of tourmaline is reported in this paper, but without extensive experimental details. The space group of tourmaline is *R3m*, and the cell of the colorless sodium, magnesium crystals from de Kalb has the dimensions $a = 15.951$ Å, $c = 7.24$ Å. This hexagonal cell has a volume of three primitive rhombohedral cells. The structure analysis shows that this kind of tourmaline has an ideal formula of $NaMg_3B_3Al_6Si_6O_{27}(OH)_4$. One such formula weight is contained in the primative rhombohedral cell, or three in the hexagonal cell whose dimensions are given.

Part of the structure of tourmaline may be described as a fragment of "Mg-kaolin." This part consists of a six-membered ring of silicon tetrahedra, each of which shares one free apex with a corner of a magnesium octahedron. The three magnesium octahedra constitute a small trigonal fragment of a brucite layer. The boron atoms occur in triangular coordination, each triangle sharing a common apex with two magnesium octahedra. This composite unit is knit to others like it by aluminum atoms, and its outer oxygen atoms are also atoms of the aluminum coordination octahedra. The alkali atoms occur sandwiched between the units along the *c* axis.

The structure not only provides excellent agreement between computed and observed diffraction intensities, but its electrostatic valence structures is very acceptable. The analyses of the tourmalines used, the coordinates of the atoms in the structure, computed and observed intensity comparison, interatomic distances, and the electrostatic bond structure are shown in tables.

INTRODUCTION

Tourmaline is one of the few common silicate crystals whose structure is not known. We have just succeeded in solving this structure, but it will be some time before our detailed account of the structure analysis can appear in print. In view of the unusual mineralogical interest in the results of our study, we thought it important to describe the structure immediately, giving sufficient intensity data to assure the critical reader that the structure is correct.

The cell and true space group of tourmaline were determined by Buerger and Parrish.[1] The space group is *R3m*. The cell edges of the Etta tourmaline on which that study was based, and referred to hexagonal axes are as follows:

$$a = 15.96 \text{ Å}$$
$$c = 7.16 \text{ Å}$$

(The original cell edges were given in *kX* units. These have been converted to Ångstrom units in the pair given above.) This hexagonal cell

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[1] Buerger, M. J., and Parrish, William, The unit cell and space group of tourmaline (an example of the inspective equi-inclination treatment of trigonal crystals): *Am. Mineral.*, **22**, 1139–1150 (1937).

contains $3\left|\begin{matrix}\mathrm{Na}\\ \mathrm{Ca}\end{matrix}\right|\mathrm{B}_3\left|\begin{matrix}\mathrm{Mg}\\ \mathrm{Al}\end{matrix}\right|_9 \mathrm{Si}_6\mathrm{O}_{27}(\mathrm{OH})_4$. This formula will be explained and corrected in subsequent discussion.

MATERIAL

For our structural study, we deliberately chose tourmalines of comparatively simple compositions. One was the white magnesian tourmaline of de Kalb, and the other was the black iron tourmaline from Andreasberg. The analyses of these are quoted in Table 1, together with the cell dimensions of the respective tourmalines obtained by semi-precision methods. The *a* axis of the de Kalb tourmaline was obtained from a back-reflection Weissenberg photograph,[2] while the other data were determined

TABLE 1. ANALYSES AND CELL DIMENSIONS OF TOURMALINES USED IN STRUCTURE INVESTIGATION

	Colorless, de Kalb, N. Y.*	Black, Andreasberg, Harz**
SiO_2	36.72%	34.01%
TiO_2	.05	.61
B_2O_3	10.81	10.89
Al_2O_3	29.86	28.80
Fe_2O_3	—	4.37
FeO	.22	13.57
MnO	—	.12
MgO	14.92	.42
CaO	3.49	.58
Na_2O	1.26	2.03
K_2O	.05	.20
Li_2O	—	.10
H_2O	2.98	2.92
F	.93	.71
Density	3.06–3.13	3.25
a	15.951 Å	16.01 Å
c	7.24 Å	7.18 Å

* Doelter, number 15, p. 751, Vol. 2, part 2. From: Penfield, S. L., and Foote, H. W., "Ueber die chemische Zusammensetzung des Turmalins": *Zeit. Krist.*, **31**, 332 (1899).

** Doelter, number 71, p. 758, Vol. 2, part 2. Analysis from Dittrich, M., and Noll, F., Inaug.-Diss., Heidelberg (**1913**) p. 22.

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[2] Buerger, M. J., The precision determination of the linear and angular constants of single crystals: *Zeit. Krist.*, (A) **97**, 433–468 (1937).

with the aid of a special back-reflection, rotating-crystal camera of 10 cm. diameter.

STRUCTURE ANALYSIS

Since our method of structure analysis will be discussed in considerable detail elsewhere, we merely outline the main features of our methods here. The locations of the dense cations were determined directly by implication methods.[3] Furthermore, the two tourmalines chosen for the structure study were deliberately selected so that their compositions were substantially identical except that one had three iron atoms where the other had three magnesium atoms. This was done so that the difference diagram[4] could be used to locate the positions of this particular replacement without any reference to the locations of the rest of the atoms.

TABLE 2. COORDINATES OF THE ATOMS IN TOURMALINE OF COMPOSITION $NaMg_3B_3Al_6Si_6O_{27}(OH)_4$ (Hexagonal Coordinates)

Atom	*Equipoint*	*x*	*y*	*z*
Na	3*a*	0	0	.770
Mg	9*b*	.133	.067	.255
B	9*b*	.117	.233	0
Al	18*c*	.050	.367	.825
Si	18*c*	.192	.192	.624
O_1=(OH)	3*a*	0	0	.403
O_2	9*b*	.058	.117	0
O_3=(OH)	9*b*	.233	.117	.032
O_4	9*b*	.142	.071	.624
O_5	9*b*	.102	.204	.742
O_6	18*c*	.200	.200	.403
O_7	18*c*	.279	.246	.758
O_8	18*c*	.058	.292	0

The rest of the structure (consisting chiefly of the locations of the oxygen atoms) was deduced from considerations of the usual coordinations of the metal atoms as well as space requirements, and supplemented by comparisons of observed intensities with those computed from trial oxygen locations. The parameters of the atoms found by these methods are shown in Table 2. That the structure they define is actually the

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[3] Buerger, M. J., The interpretation of Harker syntheses: *Jour. Appl. Phys.*, **17**, 579–595 (1946).

[4] Buerger, M. J., A new Fourier series technique for crystal structure determination: *Proc. Nat. Acad. Sci.*, **28**, 281–285, esp. 283 (1942).

correct one for tourmaline is proved by the good agreement between observed and computed intensities, which is shown in Tables 3 and 4.

TABLE 3. COMPARISON OF OBSERVED AND COMPUTED INTENSITIES FOR TOURMALINE STRUCTURE

(F's for $hk\cdot 0$, arranged in order of decreasing observed F.)

$hk\cdot 0$	Observed F	Computed F
5 5·0	139	109
2 2·0	94	78
10·1·0	83	75
6 6·0	63	68
9 0·0	57	46
4 4·0	50	45
15·0·0	50	33
7 4·0	42	50
3 0·0	41	51
9 3·0	41	47
4 1·0	41	39
10·10·0	41	40
8 2·0	35	38
16·1·0	30	29
6 0·0	28	34
11·5·0	22	20
9 6·0	20	22
15·3·0	20	13
12·0·0	17	32
8 5·0	17	24
10·4·0	17	22
8 8·0	17	19
11·2·0	10	18
9 9·0	10	10
7 1·0	10	10
3 3·0	10	10
5 2·0	10	8
11·8·0	10	5
6 3·0	0	4
1 1·0	0	1
7 7·0	0	1

TABLE 4. COMPARISON OF OBSERVED AND COMPUTED INTENSITIES FOR TOURMALINE STRUCTURE

(F's for $h0\cdot\bar{l}$ and $0k\cdot\bar{l}$, arranged in order of decreasing observed F. Computed F's not corrected for temperature.)

$hk\cdot\bar{l}$	Observed F	Computed F
5 0·1	146	136
0·10·1	116	110
6 0·3	100	89
0 0·6	87	81
0 0·3	76	78
1 0·2	59	59
9 0·0	57	47
0 6·3	50	59
15·0·0	50	54
3 0·0	41	45
0 0·9	37	34
0 4·4	36	34
0 3·3	36	30
3 0·3	33	32
0 1·4	32	35
2 0·1	32	28
6 0·0	28	31
7 0·2	20	26
2 0·4	20	22
4 0·2	17	17
0 7·1	17	17
0 4·1	17	17
0 1·1	10	9
0 2·2	0	3
8 0·1	0	3

Description of the Structure

In order to give a grasp of the main features of the tourmaline structure, it is presented in diagrammatic fashion in Figs. 1 and 2. In these illustrations the coordination polyhedrons of the silicon, magnesium, and boron atoms are emphasized. The characteristics of these polyhedra are tabulated in Table 6, and are discussed in the next paragraph. Figure 1 shows a central segment of the structure, without aluminum atoms, illustrating in some detail how the polyhedra surrounding silicon, boron, and magnesium are joined. Figure 2 shows how these central segments fit into the tourmaline structure, held together by aluminum atoms. In Fig. 2, only the bonding due to the upper set of aluminum atoms is shown.

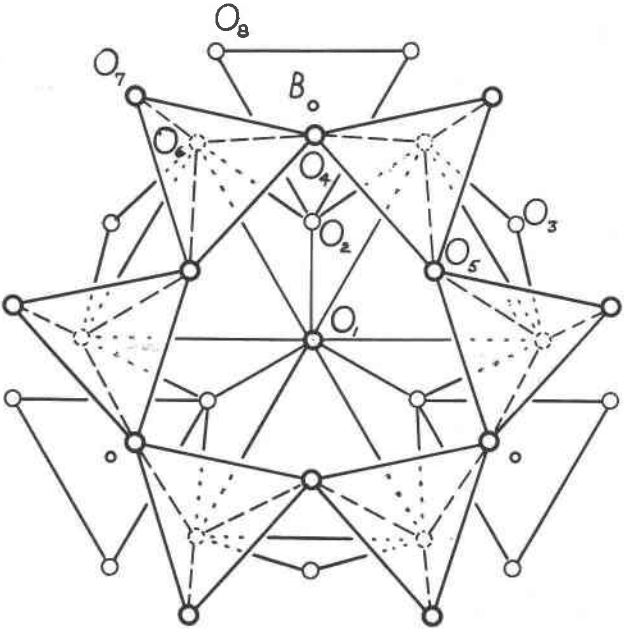

Fig. 1. "Central segment" of composition $Mg_3B_3Si_6O_{27}(OH)_4$, of the tourmaline structure, as seen looking down the *c* axis. The diagram shows the designations adopted for the oxygen atoms. All small rings represent oxygen locations, except the small ring labeled *B*, which represents a boron location. The silicon atoms are approximately in the centers of the tetrahedra, while the magnesium atoms are approximately in the centers of the octahedra.

The magnesium atoms are surrounded octahedrally by oxygen and (OH) ions, namely $O_1 = (OH)$, O_2, $O_3 = (OH)$, and O_6. The three octahedra immediately surround the 3-fold axis at the origin, and each octahedron shares an edge with each of its two equivalent neighbors. The shared ions are $O_1=(OH)$, and O_2. The magnesium atoms and their surrounding oxygen or (OH) ions thus constitute a small trigonal fragment of a brucite layer.

The six silicon atoms are surrounded tetrahedrally in the usual manner by four oxygen atoms. Each of the six tetrahedra share two of their points (O_4 and O_5) with neighboring tetrahedra to form a six-membered ring of composition Si_6O_{18}. This Si_6O_{18} ring differs from the beryl ring in not having an equatorial plane of symmetry. Instead, one of the two unshared points (O_7) is substantially in the same plane as the shared oxygens, and the other (O_6) points at right angles to this plane.

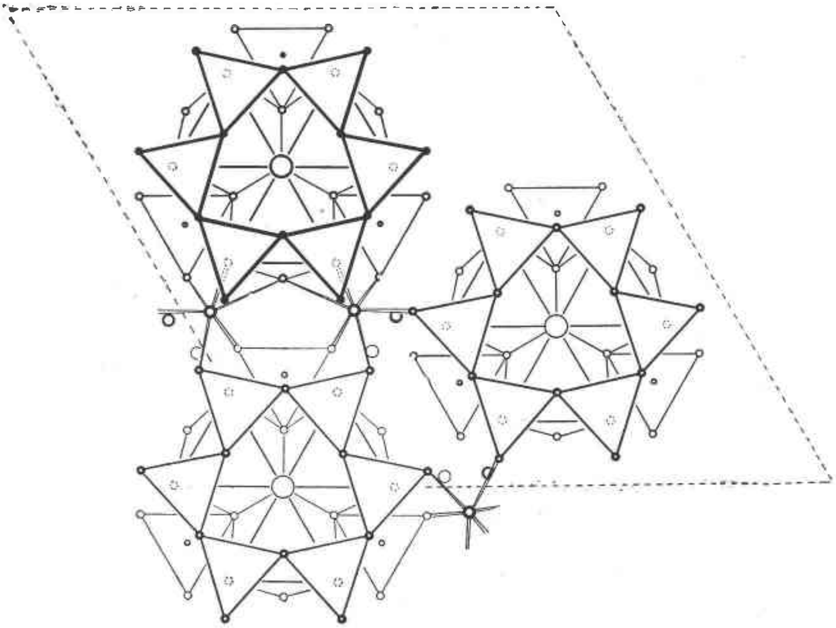

FIG. 2. Part of the tourmaline structure, as seen looking down the *c* axis. The diagram shows how three neighboring columns of "central segments" are held together by aluminum atoms. The bonding of only the uppermost aluminums is indicated. Sodium atoms are represented by the largest circles, and occur in the centers of the "central segments." The hexagonal unit cell is outlined in broken lines.

This last apical oxygen atom (O_6) is also an oxygen of the brucite fragment. The combined segment of the structure composed of the silicate ring and the brucite fragment comprises three layers of oxygen atoms in approximately cubic close-packed array, and has the formula

$Mg_3(OH)_4Si_6O_{21}$. This central core of the tourmaline structure can also be regarded as a small trigonal fragment of a "Mg-kaolin" sheet. "Mg-kaolin" is also the structure proposed by Aruja[5] for crysotile, and is also similar to part of the structure proposed by Gruner[6] for amesite.

TABLE 5. METAL-OXYGEN DISTANCES IN TOURMALINE

Metal	Number of Oxygens	Oxygen Designation	Distance
Si	1	O_4	1.55 Å
	1	O_5	1.67
	1	O_6	1.60
	1	O_7	1.60
B	1	O_4	1.58
	2	O_8	1.58
Al	1	O_3	2.23
	1	O_6	2.01
	2	O_7	2.05
	2	O_8	1.85
Mg	1	$O_1=(OH)$	2.12
	2	O_2	2.10
	1	$O_3=(OH)$	2.12
	2	O_6	2.12
Na	1	O_1	2.32
	3	O_2	2.32

The aluminum, boron, and sodium atoms, in one manner or another, serve to cement together these "central cores." The three boron atoms are each surrounded by three oxygen atoms (O_2 and O_8) in plane triangular coordination. One corner of the triangle has an oxygen (O_2) shared by two magnesium atoms, while the other two corners (O_8) are oxygen atoms outside the central $Mg_3(OH)_4Si_6O_{21}$ segment, giving a larger complex segment of composition $Mg_3B_3(OH)_4Si_6O_{27}$. The six additional oxygen atoms are part of the cubic close-packed array of oxygen atoms on substantially three levels.

The aluminum atoms are coordinated to six oxygen atoms in somewhat

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[5] Aruja, reported in "Summarized proceedings of conference on *x*-ray analysis—Oxford 1944": *Jour. Sci. Inst.*, **21,** 115–116 (1944).

[6] Gruner, John W., The kaolinite structure of amesite, $(OH)_8(Mg, Fe)_4Al_2(Si_2Al_2)O_{10}$, and additional data on chlorites: *Am. Mineral.*, **29,** 422–430 (1944).

irregular octahedral coordination, which are part of the enlarged boron-bearing unit just described. The aluminum octahedra share edges and spiral down the 3-fold screw axis. The oxygen atoms of the aluminum octahedra consist of (*a*) the points of two boron triangles, O_8, (*b*) the points of two silicon tetrahedra, C_7, and two oxygen atoms of the magnesium octahedron, O_3 and O_6. The aluminum and magnesium octahedra, therefore, share the edge O_3O_6.

TABLE 6. ELECTROSTATIC VALENCE BONDS IN TOURMALINE OF COMPOSITION $NaMg_3B_3Al_6Si_6O_{27}(OH)_4$

Bonds donated by	Bonds received by							
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8
Si				1+1	1+1	1	1	
B		1						1
Al			$\frac{1}{2}+\frac{1}{2}(-)$*			$\frac{1}{2}$	$\frac{1}{2}+\frac{1}{2}$	$\frac{1}{2}+\frac{1}{2}$
Mg	$\frac{1}{3}+\frac{1}{3}+\frac{1}{3}$	$\frac{1}{3}+\frac{1}{3}$	$\frac{1}{3}$			$\frac{1}{3}$		
Na		$\frac{1}{3}$						
Σ bonds received	1	2	$1\frac{1}{3}(-)$*	2	2	$1\frac{5}{6}$	2	2

* This Al-O bond has a length of 2.23 Å, which is greater than normal. Consequently the bond strength to be attributed to it is probably subnormal.

The sodium atoms occur on the three-fold axis, sandwiched between the central $Mg_3(OH)_4Si_6O_{21}$ segments, which are repeated in translation-equivalent fashion along the *c* axis. The sodium has an immediate coordination of three oxygen atoms and one hydroxyl ion in tetrahedral coordination.

THE COMPOSITION OF TOURMALINE

The description given above of the tourmaline structure has been arranged to bring out the geometry of the structure. In order to consider the composition of tourmaline and its variation, it is desirable to recast the description into another form.

The strengths of the bonds in a tourmaline of composition $NaMg_3B_3Al_6Si_6O_{27}(OH)_4$ decrease in the following order:

	electrostatic bond strength
Si-O B-O	1
Al-O	$\frac{1}{2}$
Mg-O, (OH)	$\frac{1}{3}$
Na-O, (OH)	$\frac{1}{3}$ or less

The bonds between the first three cations in the list, with oxygen, may be thought of as forming the frame of the structure within which there exist central pockets, which occur along the 3-fold axes. The variability of the composition of tourmaline tends not to occur in this frame. Thus, the number of silicon atoms in tourmaline closely approximates six, the number of borons is almost always exactly three, and the number of aluminums is usually $6+x$. The number x represents the number of additional aluminum atoms which may proxy for magnesium on occasion. If any variability does occur in this frame, it is chiefly in respect to a variability in aluminum. This is to be expected because the aluminum-oxygen bond strength is only $\frac{1}{2}$ as against 1 for Si-O and B-O.

The chief variability in the composition comes from the manner in which the central pocket is filled with weakly bonded cations. Since the electrostatic fields in the pocket are weak, any stray field is more or less inconsequential, and, therefore, the particular cations which enter this part of the structure are not of great importance. However, the sum of them should neutralize the interior of the pocket. Thus, the extreme center may be occupied by sodium (rarely potassium, since it is too large for the small available interstitial space) or calcium, while the three cations in the next zone must have octahedral coordination and compensate for sodium versus calcium. They may be either the monovalent lithium, divalent magnesium or iron, trivalent aluminum, iron, manganese, chromium, etc., in such a collection that the contents of the central pocket remains a self-neutralizing collection.

Finally, we wish to point out that the electrostatic valence rule is satisfied in the structure of tourmaline. This is shown in Table 6.