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A Fourier Analysis of the Structure of Tourmaline

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The crystal structure of tourmaline, (Na, Ca) (Li, Al)$_3$Al$_6$(OH)$_4$(BO$_3$)$_3$Si$_6$O$_{18}$, has been revised using the Fourier-synthesis method. The structure is little different from that originally proposed and described by the present writers. A few minor changes in atomic positions have improved some of the interatomic distances as well as the co-ordinations of atoms. A comparison has been made with the structure arrived at by Donnay & Buerger, from which the present structure differs in the precise configuration of the Si$_6$O$_{18}$ group.

Introduction

In spite of its general interest (e.g. Bragg, 1937), the crystal structure of tourmaline remained unknown until Hamburger & Buerger (1948) recently worked out its main features. Applying the implication method (Buerger, 1946), they arrived at a very reasonable scheme for the structure. Unaware of the progress of their work we, too, undertook several years ago an X-ray study of this mineral, and by means of the usual trial-and-error method we obtained a structure of which the detailed report has been printed only lately (Ito, 1950), although a brief account of it was given as early as 1947 (Sadanaga, 1947).

The two proposed structures are essentially the same, containing similar Si$_6$O$_{18}$ and BO$_3$ groups, and both check apparently well with the experimental data. There seem to exist nevertheless between them certain differences. In order to settle them we undertook a further investigation of tourmaline in which, contrary to our previous study, the Fourier-synthesis method has been exclusively resorted to. In the meantime, while the manuscript of the present paper was being submitted to the editor of this journal, the same authors gave the final and more elaborate account of their results (Donnay & Buerger, 1950).

Experimental

The specimens examined are rose-coloured rubellite from Brazil, having the composition

(Na, Ca) (Li, Al)$_3$(Al, Fe, Mn)$_6$(OH)$_4$(BO$_3$)$_3$Si$_6$O$_{18}$,

with the probable atomic ratios

Na : Ca = 7 : 1, Li : Al = 1 : 2

and Al : Fe : Mn = 6 : 0·1 : 0·1.

The unit cell has the dimensions

$a = 16{\cdot}0$, $c = 7{\cdot}17$ A. (Mo $K\alpha$, $\lambda = 0{\cdot}71$ A.)

There are three molecules of the above formula in the hexagonal unit cell. The space group is C_{3v}^5–$R3m$ (Buerger & Parrish, 1937).

All the experimental data for the present study, except for a few reflexions whose intensities have been corrected, are the same as those used previously. They were obtained from photographic and ionization-spectrometer measurements. The intensity values, obtained by applying the multiple-film technique to the Weissenberg–Buerger photographs (Mo, Cu and Co $K\alpha$), were converted into absolute intensities by correlating them with the values obtained with the ionization spectrometer (Mo $K\alpha$; rocksalt (400) as standard). All the spectrometer measurements were made in 1945 by H. Sawada and Y. Takéuchi of this Laboratory.

Preliminary refinement of atomic positions

For the possible rapid convergence in the course of successive approximation of the contour lines in the Fourier projection a further refinement of atomic positions was undertaken. Re-examining the interatomic distances given by us (Ito, 1950, p. 141), we find that in our structure the possibility of adjustment of atomic positions lies in the first place in those of the BO$_3$ groups, for which the O–O distance is 2·8 A. instead of the usual 2·4 A. Accordingly, by shifting their positions and also those of Al, which has a more or less distorted co-ordination, and of (Li, Al), and comparing extensively the calculated and observed F values, we obtained a new set of parameters for beginning the Fourier synthesis (Table 1, columns (1)). We note that this tentatively revised structure is little different from our original one (Ito, 1950, p. 138).

Fourier synthesis

For the xy Fourier projection the following summation was carried out:

$$\rho_{xy0} = \frac{1}{A}[F_{000} + 2\Sigma\Sigma \mid F_{hk0} \mid \cos\{2\pi(hx+ky) - \alpha(hk0)\} + 2\Sigma\Sigma \mid F_{h\bar{k}0} \mid \cos\{2\pi(hx-ky) - \alpha(h\bar{k}0)\}].$$

In the synthesis $61 \times 3 + 1 = 184$ terms derived from the observed ($hk.0$) reflexions were summed with the

calculated phase angles, covering one-third of the unit cell with more than 1000 evaluated points. (The a axis was subdivided into 100 parts giving intervals of 0·16 A.) By the usual procedure of successive approximation we obtained in the fifth synthesis a well-defined Fourier map of electron density in which the peaks coincide with the atomic positions finally chosen (Fig. 1 (*a*)).

As usual, the reflexions observable on the Weissenberg photographs are practically limited to those with $Q=4\sin^2\theta/\lambda^2 < c.\ 1{\cdot}70$ A.$^{-2}$, whether we use Mo or Cu (or Co) radiations, whereas with the ionization spectrometer and with Mo radiation the Q value ranges easily up to 5·00 A.$^{-2}$. Therefore, in the synthesis, the (h0.0) and (hh.0) spectra measured with the spectrometer were cut off at orders higher than (18.0..0) or (11.11..0) respectively, for which the Q values are 1·680 and 1·883 A.$^{-2}$. Moreover, we not only thus rejected the unnecessary higher-order reflexions but also multiplied all the available experimental F values (photographic and spectrometric) by a Debye–Waller (temperature) factor, $\exp[-B(\sin/\lambda)^2]$, choosing for B a value, namely, 1·5 A.^{2}, that reduces the F values of the limiting reflexions to half the observed values. These precautionary measures were deemed necessary to avoid in the synthesis the complications that might arise from the uneven distribution of spectra over the range of experiment and to reduce to a minimum the effect of the arbitrary and abrupt termination of the Fourier series.

In order to insure the accuracy of the determination of the z parameters we further carried out a one-dimensional summation along [00.1], using (00.l) spectra, and compared the result with the curve obtained after Alston & West (1928) by synthesis of the theoretical linear electron density of the component individual atoms, each placed in the assigned position (Fig. 2). The curves for the linear electron density of atoms, being usually not available in the literature, were drawn specially for this purpose by 'analysing' (Fourier) an arbitrarily chosen hypothetical structure. This can be done because, given a set of parameters, we can calculate from the atomic f values the F values of the arrangement they define. We have used the atomic f values given in the *International Tables*, adopting, to conform with the actual composition of the specimens examined, the following modifications:*

$$f(\mathrm{Na,\ Ca}) = \tfrac{1}{8}\{7f(\mathrm{Na^+}) + f(\mathrm{Ca^{2+}})\},$$

$$f(\mathrm{Li,\ Al}) = \tfrac{1}{3}\{f(\mathrm{Li^+}) + 2f(\mathrm{Al^{3+}})\},$$

$$f(\mathrm{OH}) = \{f(\mathrm{O^{2-}}) + f(\mathrm{F^-}) - f(\mathrm{F})\}.$$

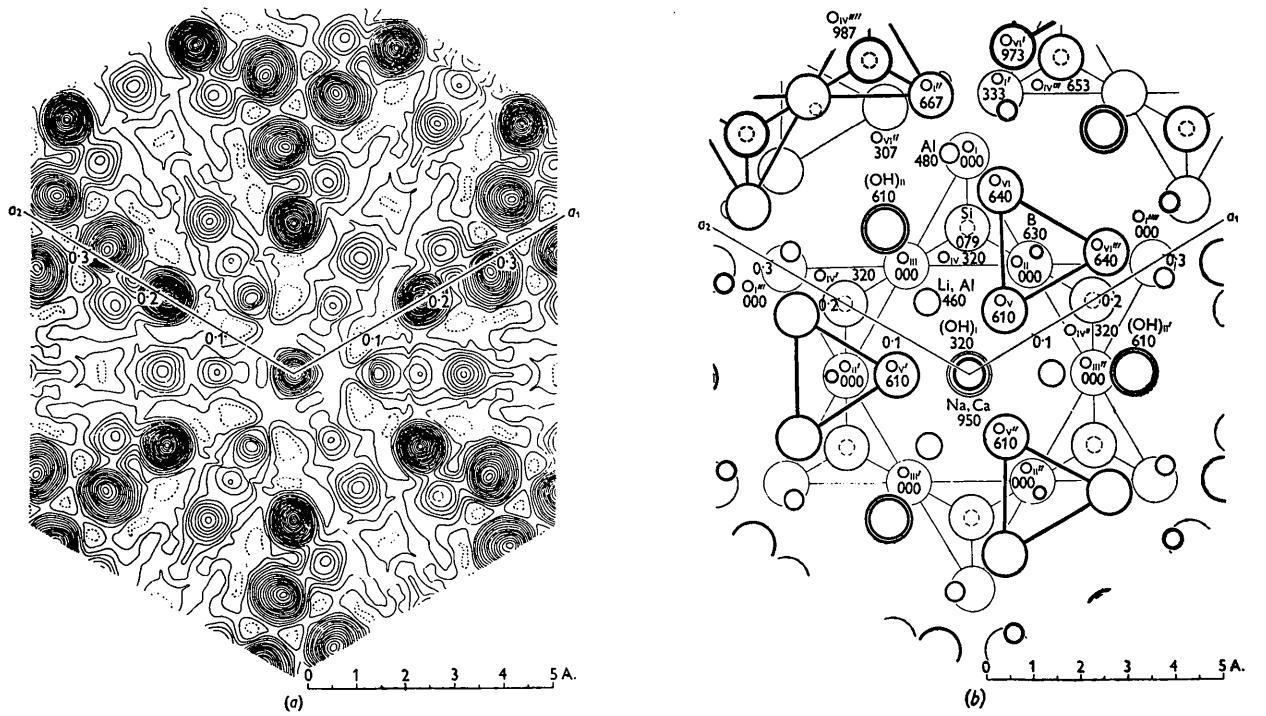

Fig. 1. (*a*) Fourier projection of electron density on (00.1). Contours at intervals of 2 e.A.$^{-2}$, zero-electron lines being broken. (*b*) The structure projected on (00.1). Numbers give the height of each atom as a permillage of the c translation (7·17 A.). An Si_6O_{18} and three BO_3 groups are traced by thin and thick lines respectively. Part of the Si_6O_{18} groups $\frac{1}{3}c$ and $\frac{2}{3}c$ above that fully depicted are represented by medium-thick and thick lines. Only a portion of the unit cell is shown.

Results

The parameters thus redetermined are given in Table 1, columns (2), and the revised structure is illustrated in Fig. 1 (*b*). In Table 2 are listed the calculated F values

* The presence of Fe and Mn replacing Al has been neglected.

Table 1. *Co-ordinates of atoms*

Atom	No. of atoms in the unit cell	*x/a* (1)	*x/a* (2)	*y/b* (1)	*y/b* (2)	*z/c* (1)	*z/c* (2)
Na, Ca	3	0	0	0	0	0·950	0·950
Li, Al	9	0·063	0·063	0·125	0·125	0·460	0·460
Al	18	0·254	0·270	0·297	0·297	0·480	0·480
Si	18	0·188	0·188	0·188	0·188	0·084	0·079
B	9	0·208	0·208	0·104	0·104	0·630	0·630
O_I	18	0·288	0·280	0·288	0·280	0	0
O_{II}	9	0·188	0·188	0·094	0·094	0	0
O_{III}	9	0·094	0·094	0·188	0·188	0	0
O_{IV}	18	0·188	0·188	0·188	0·188	0·320	0·320
O_V	9	0·110	0·110	0·055	0·055	0·610	0·610
O_{VI}	18	0·260	0·260	0·202	0·210	0·640	0·640
$(OH)_I$	3	0	0	0	0	0·320	0·320
$(OH)_{II}$	9	0·125	0·125	0·250	0·250	0·610	0·610

(1) Initial co-ordinates from which the Fourier refinement was started.
(2) Final co-ordinates.

Table 2. *Intensities of reflexions*

(*a*) Measurements with the ionization spectrometer (Mo $K\alpha$, $\lambda = 0{\cdot}71$ A.; rock-salt (400) as standard).

hk.l	F_o	F_c	α (°)
00.0		1419·6	
30.0	83·0	94·0	7·5
60.0	104·8	108·9	337·1
90.0	161·7	111·5	104·0
12.0..0	82·5	88·3	98·1
15.0..0	102·7	132·7	9·6
18.0..0	51·1	22·7	319·8
21.0..0	70·0	122·2	335·2
24.0..0	30·8	45·1	235·4
27.0..0	74·7	51·4	354·1
30.0..0	72·9	23·7	326·9
11.0	50·9	10·8	180·0
22.0	162·3	227·8	180·0
33.0	50·2	64·6	0
44.0	127·5	109·9	0
55.0	198·0	242·1	0
66.0	168·8	174·6	0
77.0	44·4	85·7	0
88.0	47·4	66·5	180·0
99.0	49·1	6·2	180·0
10.10..0	85·9	94·0	0
11.11..0	105·2	154·7	0
12.12..0	67·7	20·2	0
13.13..0	44·7	16·8	0
14.14..0	0	7·0	180·0
15.15..0	0	11·8	0
16.16..0	74·0	120·0	0
17.17..0	92·0	19·3	0
18.18..0	47·1	24·7	0
00.3	246·0	292·2	13·4
00.6	191·8	260·3	291·8
00.9	56·3	62·1	278·5
0.0..12	91·0	122·0	305·9
0.0..15	51·7	106·5	36·8

(*b*) Intensities estimated visually in Weissenberg photographs (Mo, Cu and Co $K\alpha$) and correlated with those measured with the ionization spectrometer.

hk.l	F_o	F_c	α (°)
14.0	108	110·3	354·7
25.0	45	41·9	245·0
17.0	59	50·0	122·1
36.0	72	53·2	211·0
28.0	124	81·1	131·7
47.0	151	166·4	21·4
1.10..0	184	222·7	20·2
39.0	167	161·9	214·1
58.0	77	50·0	203·7
2.11..0	44	43·7	95·5
4.10..0	43	42·2	339·2
69.0	49	42·8	331·1
1.13..0	59	58·8	153·7
3.12..0	71	64·0	235·2
5.11..0	107	100·7	12·8
7.10..0	41	34·2	343·0
2.14..0	29	27·2	25·7
4.13..0	47	44·5	264·2
6.12..0	36	23·7	2·2
3.15..0	34	42·1	59·3
8.11..0	55	67·9	191·0
1.16..0	89	111·8	346·6

(*c*) Intensities estimated in Weissenberg–Buerger photographs (Co $K\alpha$, $\lambda = 1{\cdot}79$ A.). Only part of observed reflexions are given.

hk.l	*I*	F_c	α (°)
50.$\bar{1}$	*vvs*	337·8	316·2
30.3	*m*+	144·0	212·0
30.$\bar{3}$	*w*	77·3	219·6
70.1	*w*	99·8	122·3
60.3	*w*	82·4	202·6
60.$\bar{3}$	*vs*	290·8	299·5
80.$\bar{1}$	—	16·3	179·8
10.0..1	*vs*	229·8	33·2
40.$\bar{5}$	*s*	131·7	228·8
50.5	*vs*	238·4	209·0
11.0..$\bar{1}$	*s*	208·0	336·3
21.1	*m*−	70·6	221·6
21.$\bar{2}$	*s*	147·3	121·5
51.1	*s*	162·6	48·8
11.3	—	55·1	317·7
11.$\bar{3}$	—	55·1	42·3
51.$\bar{2}$	*s*	197·3	156·7
41.3	—	52·1	359·9
41.$\bar{3}$	*w*	141·3	349·6
31.$\bar{4}$	—	74·2	59·4
61.2	—	90·2	331·8
51.4	*s*	220·6	101·2
51.7	*m*	100·0	219·7
32.1	*w*	56·2	298·8
42.$\bar{1}$	*w*	53·3	7·6
32.4	*m*	117·2	214·5
22.3	*s*	112·4	264·0
22.$\bar{3}$	*s*	112·4	96·0
62.1	*m*+	55·2	258·8
42.$\bar{4}$	*w*	64·8	258·0
13.1	*m*	67·4	221·0
43.1	*m*+	106·5	309·9
43.$\bar{2}$	*s*	250·3	20·4
53.$\bar{1}$	*vw*	58·8	277·8
33.3	*m*+	103·2	299·7
33.$\bar{3}$	*m*+	103·2	60·3
53.2	*w*	18·9	83·5
73.$\bar{2}$	*vw*	50·1	47·6
43.4	*s*	251·7	325·2
73.4	—	77·9	315·5
10.3..$\bar{2}$	—	26·5	143·8

Table 3. *Comparison of interatomic distances in tourmaline*

Ito & Sadanaga			Donnay & Buerger		
Atom	Neighbour	Distance (A.)	Atom	Neighbour	Distance (A.)
Si	O_I	1·59	Si	O_7	1·61
	O_{II}, O_{III}	1·61		O_4	1·61
				O_5	1·58
	O_{IV}	1·72		O_6	1·50
B	O_V	1·37	B	O_2	1·63
	O_{VI}, $O_{VI'''}$	1·47		O_8, $O_{8''}$	1·65
Li, Al	O_{IV}, $O_{IV'}$	2·02	Mg	O_6, $O_{6'}$	2·24
	O_V, $O_{V'}$	1·95		O_3, $O_{2'}$	2·06
	$(OH)_I$	2·01		O_1=(OH)	2·18
	$(OH)_{II}$	2·04		O_3=(OH)	2·08
Al	$O_{I'}$	1·97	Al	O_7*	2·26
	$O_{I''}$	1·86		$O_{7'}$	1·98
	O_{IV}	1·95		O_6	1·84
	O_{VI}	1·76		O_8	1·72
	$O_{VI''}$	2·08		O_8†	1·67
	$(OH)_{II}$	2·25		O_3=(OH)	2·66
Na. Ca	O_{II}, $O_{II'}$, $O_{II''}$, O_{III}, $O_{III'}$, $O_{III''}$	2·64	Na, Ca	O_4, $O_{4'}$, $O_{4''}$	3·00
				O_5, $O_{5'}$, $O_{5''}$	2·92
	O_V, $O_{V'}$, $O_{V''}$	2·88		O_2, $O_{2'}$, $O_{2''}$	2·23
	$(OH)_I$	2·65		O_1=OH	3·41
O_I	$O_{I'}$, $O_{I''}$	2·81	O_7	O_7*, $O_{7'}$	3·41
	O_{II}, O_{III}	2·58		O_4	2·57
	O_{IV}	2·77		O_5	2·68
	$O_{IV''''}$	3·20		O_6	2·82
	O_{VI}	2·76		$O_{6'''}$	2·82
	$O_{VI'}$	2·60		O_8	2·57
	$O_{VI''}$	2·99		$O_{8'}$	2·46
	$(OH)_{II'}$	2·98		O_8†	2·88
				$O_{3'}$=OH	3·44
O_{II}	O_{III}, $O_{III''}$	2·62	O_4	O_5, $O_{5''}$	2·51
	O_{IV}, $O_{IV''}$	2·75		O_6, $O_{6''}$	2·55
	O_V	3·00		O_2	3·13
O_{III}	O_{IV}, $O_{IV'}$	2·75	O_5	O_6, $O_{6'}$	2·22
	$(OH)_{II}$	2·95		O_3=OH	3·18
O_{IV}	$O_{IV'}$, $O_{IV''}$	3·02	O_6	$O_{6'}$, $O_{6''}$	3·12
	O_V	2·78		O_2	2·98
	O_{VI}	2·52		O_8	2·60
	$O_{VI''}$	3·06		O_8†	2·56
	$(OH)_I$	3·02		O_1=OH	3·12
	$(OH)_{II}$	2·71		O_3=OH	3·18
O_V	$O_{V'}$, $O_{V''}$	2·64	O	$O_{2'}$, $O_{2''}$	2·77
	O_{VI}, $O_{VI'''}$	2·46**		$O_{8''}$, O_8	2·79**
	$(OH)_I$	2·58		O_1=OH	2·78
	$(OH)_{II}$, $(OH)_{II''}$	3·02		O_3=OH, $O_{3''}$=OH	2·83
O_{VI}	$O_{VI'''}$	2·57**	O_8	$O_{8''}$	2·96**
	$(OH)_{II}$	2·56		O_3	2·71

Some of the distances in Donnay & Buerger's structure have been corrected by recalculation on the basis of the co-ordinates given. Primes denote equivalent atoms. * and † denote the atom in the molecule about lattice points ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3}$) and ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{2}{3}$) respectively (after Donnay & Buerger). ** denotes oxygen distances in the BO_3 group.

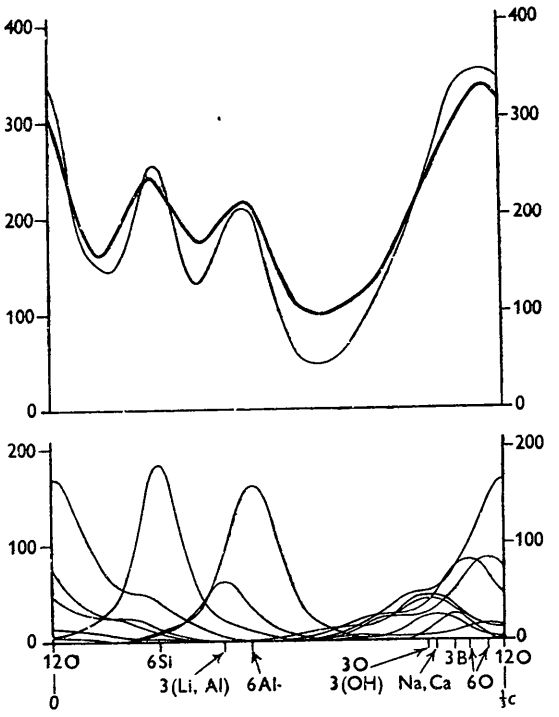

Fig. 2. One-dimensional Fourier diagram along [00.1]. The thick curve shows the result of synthesis, obtained using experimental F values; the thin curve shows the theoretical linear electron density, obtained by summing those of the component atoms, each in its assigned position, as shown in the lower part of the figure.

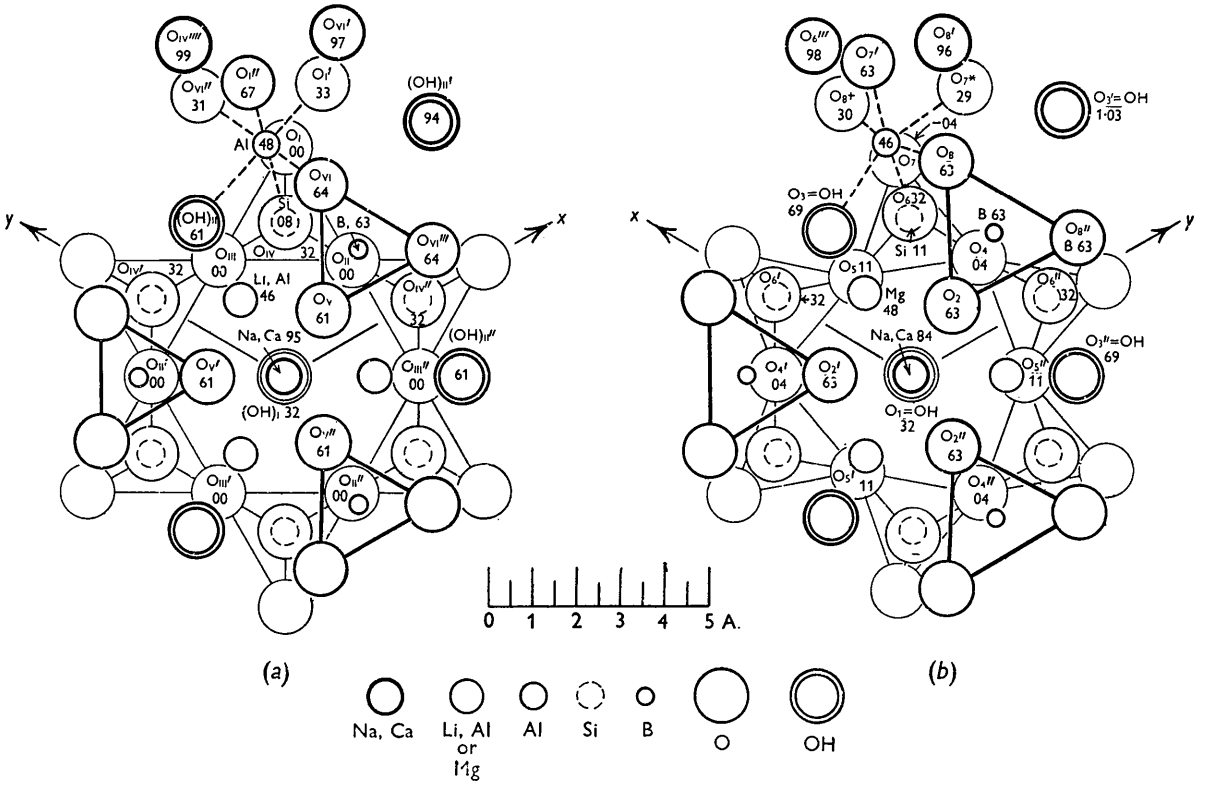

Fig. 3. The structure of tourmaline (in part) projected on (00.1) (*a*) after the present writers, (*b*) after Donnay & Buerger. Numbers give the height of each atom in the cell as a percentage of the **c** translation (7·17 A. in (*a*) and 7·24 A. in (*b*)), boron atoms being placed on the same level ($z/c = 0{\cdot}63$) in both (*a*) and (*b*). An Si_6O_{18} and three BO_3 groups are traced by thin and thick full lines. Bonds around Al are represented by broken lines.

for the revised structure for comparison with the experimental F values and also with some of the intensities visually estimated in the photographs.

This revision by the Fourier method confirms in nearly every respect the structure originally proposed and described by the present writers (Ito, 1950, p. 130). A few minor shifts in atomic positions, however, have considerably contributed to the improvement of interatomic distances (Table 3). The co-ordination, too, has undergone little change, the only notable difference being that around the aluminium atoms, which now occupy the middle of a fairly regular octahedron (less distorted than previously described), formed of five oxygen atoms and one OH group.

Comparison with Donnay & Buerger's structure

Given the prior publication of Donnay & Buerger's work on tourmaline, it may be appropriate to compare their results with ours. We give in Fig. 3 the structure of tourmaline in Donnay & Buerger's and our versions, both projected on (00.1). To facilitate comparison atoms are projected in a similar way (cf. Fig. 1 (*b*)), and boron atoms are placed on the same level.

As Donnay & Buerger observed, their determination agrees roughly with ours. The two structures are both composed of the Si_6O_{18} (ring) and BO_3 (triangle) groups held together by (Li, Al) or Mg, (Na, Ca), Al and OH. The similarity is such that the relative positions in the unit cell of almost all atoms and atom groups are practically the same.

Once, however, we come to examine the structures in detail, and particularly the configuration of the Si_6O_{18} group, a difference emerges. Whereas the ring in Donnay & Buerger's structure is *ditrigonal* in symmetry and rather rugged in shape, it is in our structure *hexagonal* and quite regular, with the 'basal' triangles of its component six oxygen tetrahedra lying perfectly in a plane. Our Si_6O_{18} ring may actually be conceived as a dismembered hexagon from the Si_4O_{11} chain in amphibole or the Si_2O_5 sheet in mica. Notwithstanding this difference, silicon atoms and those oxygen atoms which occupy the 'apices' of the tetrahedra are arranged in Donnay & Buerger's (as well as our) structure in a nearly hexagonal fashion. Further, Donnay & Buerger placed five oxygen atoms and one OH group in an irregular form around aluminium, in sharp contrast with the fairly regular octahedral arrangement of these atoms in our (revised) structure.

The environment of (Na, Ca) is peculiar and unusual in both structures. In our structure (Na, Ca) has ninefold co-ordination, being surrounded by three oxygen atoms, one each from three BO_3 groups, and by six more oxygen atoms as the nearest neighbours. Donnay & Buerger gave to the same atom a fourfold co-ordination with three oxygen atoms and one OH group arranged tetrahedrally.

Only (Li, Al) or Mg, occupying approximately the same positions in both structures, has a co-ordination identical in form and character, being situated in the middle of a regular octahedron formed of four oxygen atoms and two OH groups.

Table 3 shows a comparison of the interatomic distances in the two structures.

References

Alston, N. A. & West, J. (1928). *Z. Krystallogr.* **69**, 149.

Bragg, W. L. (1937). *Atomic Structure of Minerals.* Ithaca: Cornell University Press.

Buerger, M. J. (1946). *J. Appl. Phys.* **17**, 579.

Buerger, M. J. & Parrish, W. (1937). *Amer. Min.* **22**, 1139.

Donnay, G. & Buerger, M. J. (1950). *Acta Cryst.* **3**, 379.

Hamburger, G. E. & Buerger, M. J. (1948). *Amer. Min.* **33**, 532.

Ito, T. (1950). *X-ray Studies on Polymorphism.* Tokyo: Maruzen.

Sadanaga, R. (1947). *J. Geol. Soc. Tokyo*, **53**, 52.