THE UNIT CELL AND SPACE GROUP OF TOURMALINE (AN EXAMPLE OF THE INSPECTIVE EQUI-INCLINATION TREATMENT OF TRIGONAL CRYSTALS)

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Abstract

The inspective equi-inclination treatment of hexagonal crystals in general is outlined. The lattice type may be determined with great ease merely by inspecting an appropriate n-level equi-inclination photograph. The reciprocal relations in the hexagonal system are also discussed. These are vital to an accurate unit cell determination and have not previously been discussed in this connection.

Two previous investigations have assigned tourmaline to space groups based upon a hexagonal lattice. This equi-inclination study plainly shows that it is based rather upon a rhombohedral lattice. The space group is unequivocally determined. The cell data for tourmaline from the Etta Mine, South Dakota, are as follows:

Diffraction symbol: 32/m R3 – –
Lattice: rhombohedral
Crystal class: C_{3v}
Space group: C_{3v}^5, R3m

Cell dimensions:	rhombohedral	referred to simplest hexagonal cell
	$a=9.500$ Å	$A=15.928$Å
	$\alpha=66°05'$	$C=7.151$
		$C/A=0.4490$

Formula weights of

$$\left|\begin{matrix}Na\\Ca\end{matrix}\right|R_3\left|\begin{matrix}Al\\Fe\end{matrix}\right|_6 B_3Si_6O_{27}\left|\begin{matrix}O\\OH\\F\end{matrix}\right|_4$$

per cell:	1	3

Introduction

The unit cell and space group of tourmaline were first investigated by Miss Kulaszewski,[1] who based her studies mainly on Laue photographs made from thin slips cut parallel to (0001), (10$\bar{1}$1), (50$\bar{5}$2), (01$\bar{1}$1), (10$\bar{1}$0), and (11$\bar{2}$0). These photographs were supplemented by oscillation spectrograms from these same slips, made with MoK radiation. She gives the following cell dimensions, referred to hexagonal axes, for clear rose-red tourmaline from Pennig, Saxony:

$$a = 16.23\text{Å}$$
$$c = 7.26$$

[1] Kulaszewski, Charlotte, Über die Kristallstruktur des Turmalins: *Abhandl. math-phys. Kl. Sächn. Akad. Wissen.*, vol. **38**, 1921, included in Rinne, Friedrich: *Röntgenographische Feinbaustudien*, **4**, pp. 83–117.

Miss Kulaszewski's indexing of reflections (a monumental undertaking compared with the ease of attaining the required information by the inspective equi-inclination method) shows fulfillment of the analytical condition for the rhombohedral lattice,

$$\frac{h-i-l}{3} = \text{an integer},$$

by only 41% of the indices of reflections recorded from spectrograph photographs and by only 48.5% of those recorded from the Laue photographs. She accordingly selected the hexagonal lattice as the correct one for tourmaline. On the basis of reflection data, she assigned this mineral to either space group C_{3v}^1 or C_{3v}^2, between which it was impossible to distinguish.

These results were confirmed by Machatschki,[2] who employed the rotation method and the spectrometer method. Molybdenum radiation was used with the latter technique but no statement of the radiation used with the rotation method is given. He records the following axial data:

	Black tourmaline, Grundesund, Söndeled, Norway.	Pale red alkaline-earth tourmaline, San Diego, California.	Pale red tourmaline, Pala, California.
$a=$	16.02 Å	15.81 Å	15.87 Å
$c=$	7.22	7.10	7.13

Machatschki agrees with Miss Kulaszewski in finding many reflections eliminating a rhombohedral lattice, but with the proviso that the indexing of the reflections is somewhat uncertain due to the extreme length of the a-axis. The hexagonal cell contains 3 formula weights of $XY_9B_3Si_6H_xO_{31}$. Space groups C_{3v}^3 and C_{3v}^4 are eliminated on the basis of the appearance of odd orders of the basal reflection. Since the crystal class C_{3v} only has the six space groups $C_{3v}^{1,2,3,4,5,6}$, the last two of which are based upon a rhombohedral lattice, Machatschki implicitly agrees with Kulaszewski in assigning tourmaline to the two uneliminated hexagonal space groups C_{3v}^1 or C_{3v}^2, with the proviso mentioned.

Dr. J. D. H. Donnay called the attention of one of the writers to the fact that while the x-ray investigations of tourmaline had apparently assigned the crystal to a hexagonal lattice, the surface development points to a rhombohedral lattice, and he suggested that this discrepancy be investigated here by the equi-inclination[3,4,5] Weissenberg method. A

[2] Machatschki, Felix, Die Formeleinheit des Turmalins: *Zeits. Krist.*, (A) vol. **70**, pp. 224–228, 1929.

[3] Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs: *Zeits. Krist.*, (A) vol. **88**, pp. 356–380, 1934.

reinvestigation of the unit cell and space group of tourmaline was accordingly undertaken. Since hexagonal crystals have not been previously treated by the inspective method,[4] this investigation constitutes a type case for the determination of the cell characteristics of crystals of this system without indexing procedure.

Material

The writers are indebted to Dr. Harry Berman of Harvard University for the gift of a number of suitable tourmaline crystals from the Etta Mine, South Dakota. This material consists of small crystals, less than 1 mm. long, and of about $\frac{1}{4}$ mm. in cross sectional diameter. The habit tends towards hexagonal prisms, without well-developed terminal faces. The refractive indices are as follows:

$$\omega = 1.658 \pm .002$$

$$\epsilon = 1.633 \pm .002$$

$$\omega - \epsilon = .025$$

While neither density nor analysis is available for this material, a density of 3.09 is suggested by a comparison of these optical properties with those compiled by Larsen and Berman.[6]

Method

The general methods have already been described.[3,4,5] Unfiltered copper radiation from a Hadding x-ray tube was employed.

The Crystal Class

The c-axis, 0-layer equi-inclination photograph displays the plane symmetry[4] C_{6l}, while the n-level photographs all display the plane symmetry C_{3l}. 0-layer photographs about each of the two possible hexagonal a-axes display the plane symmetries C_{2l} and C_2, respectively. These data fix the centro-symmetrical point-group as D_{3d}. These x-ray data permit the symmetry of tourmaline to be either C_{3v}, D_3, or D_{3d}. The absence of two-fold axes in the morphological development and other physical properties of tourmaline crystals definitely fixes the correct crystal class as C_{3v}.

[4] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeits. Krist.*, (A) vol. **91**, pp. 255–289, 1935.

[5] Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs: *Zeits. Krist.*, (A) vol. **94**, pp. 87–99, 1936.

[6] Larsen, Esper S., and Berman, Harry, The microscopic determination of the non-opaque minerals: *U. S. Geological Survey, Bull.* **848**, p. 248, 1934.

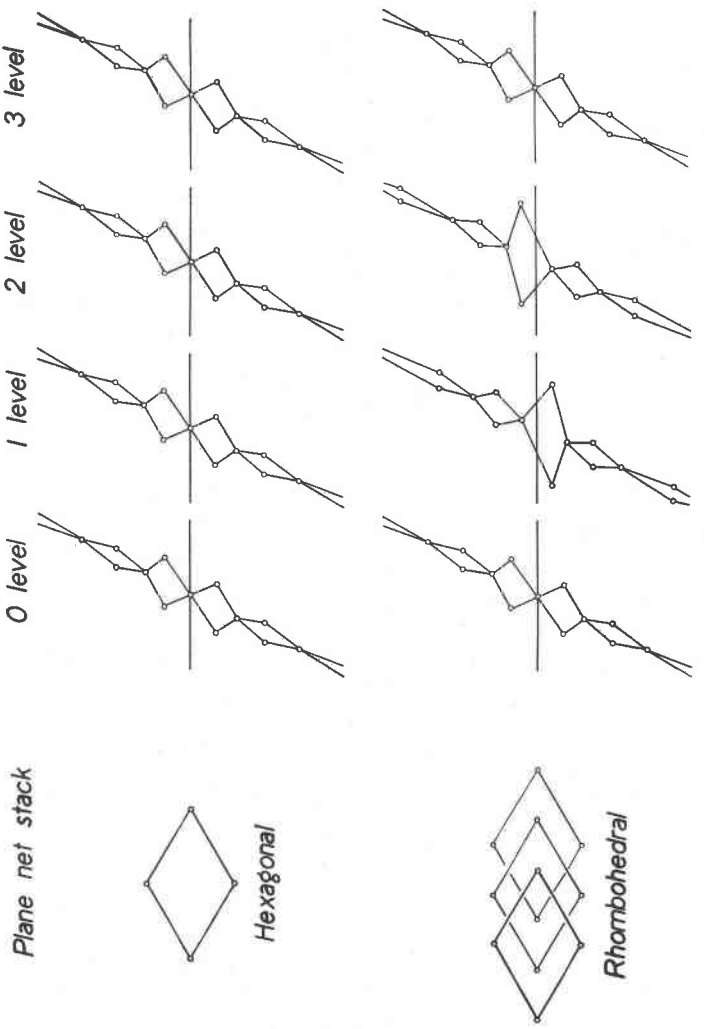
Plane net stack
0 level
1 level
2 level
3 level
Hexagonal
Rhombohedral

FIG. 1

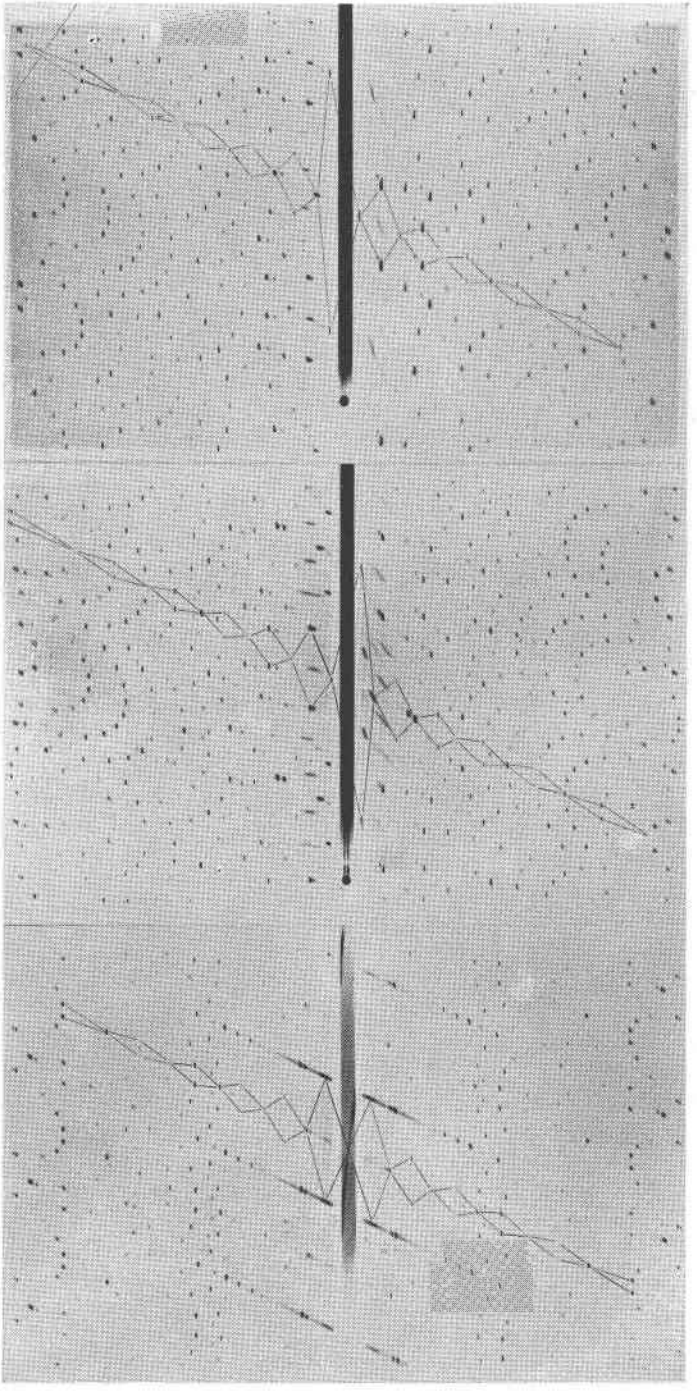

FIG. 4

FIG. 3

FIG. 2

The Space Lattice Type

A c-axis rotation photograph provides a rough estimate of the identity period along this axis, which in the case of the Etta tourmaline proved to be about 7.03 Å long. With this unrefined value, the equi-inclination settings and screen settings may be found.[5] A series of equi-inclination photographs for rotations about the c-axis permit one to resolve the reciprocal lattice into stacks of plane reciprocal lattices normal to the c-axis.[4] The analysis of this stacking unequivocally fixes the space lattice type. Both the hexagonal and rhombohedral lattices consist of stacks of equilateral triangular nets normal to the c-axis. In the case of the hexagonal lattice, the nets project on a plane parallel with the net plane in exactly superposed position, Fig. 1. In the case of the rhombohedral lattice they project in such a way as to be displaced by $\frac{1}{3}$ of a long mesh-diagonal for each succeeding layer. The equi-inclination Weissenberg projections of these layer sequences are unique, and characteristic portions are shown in Fig. 1. The displacement of the cells in the rhombohedral case is along one of the two nonequivalent position-symmetry lines of the photograph of the zero layer, or along the one set of unique position-symmetry lines of the n-layers. Figure 1 illustrates the point (reflection) environment of this line for the hexagonal and rhombohedral cases.

In Figs. 2, 3 and 4 are illustrated the equi-inclination photographs for the c-axis rotation in the case of tourmaline. The conditions plainly correspond with those illustrated for the rhombohedral lattice in Fig. 1. Tourmaline is accordingly based upon a rhombohedral, not a hexagonal lattice.*

The Space Group

There are only two possible space groups for a crystal having the point group symmetry C_{3v} and based upon a rhombohedral lattice, namely C_{3v}^5 and C_{3v}^6. The differences between these, and the criteria to be sought in distinguishing them, are plainly indicated by their orientation symbols $R3m$ and $R3c$ respectively. In the first case the vertical symmetry planes appear as mirror planes, in the second case, they appear with glide component $c/2$. To distinguish between them it is merely necessary to investigate the character of the symmetry plane, which is done by comparing the 0- and n-level reciprocal lattice planes parallel with it. If these have identical translations, a mirror plane is indicated, while if the c

* Since this conclusion was at variance with earlier results, we also took the trouble to reconstruct[3] the reciprocal lattice for a 180°ω range for the 0, 1, 2, and 3 levels. The reciprocal lattice so obtained confirms the conclusion that the direct lattice of tourmaline is rhombohedral.

translation is doubled on the 0-level, a glide plane with glide component $c/2$ is indicated.

In the case of tourmaline, the former condition proves to be the case, which unequivocally fixes the space group for tourmaline as C_{3v}^5, $R3m$.

Reciprocal Relations in the Hexagonal System

Cell dimensions of rhombohedral crystals are conveniently derived by first referring the crystal to hexagonal coordinates and then transforming to rhombohedral coordinates. A knowledge of the relations between reciprocal and direct lattices is of fundamental importance in the determination of the dimensions of the direct lattice. These relations have been discussed from this viewpoint for all important cases[7] except the hexagonal ones.

The reciprocal relations for the hexagonal system are illustrated in Fig. 5. It will be observed that the reciprocal of a hexagonal lattice is another hexagonal lattice whose orientation is rotated 30° from that of the first. The reciprocal of a hexagonal coordinate system to which a rhombohedral crystal has been referred, however, is another hexagonal coordinate system of identical orientation. This is to be expected because the reciprocal of a rhombohedral lattice is another rhombohedral lattice of different dimensions but identical orientation.

The determination of the length of a direct cell axis consists of:

(1) Measurements of the film equivalents of one or more reciprocal axes.
(2) The calculation of the actual reciprocal axes from these measurements.
(3) The transformation of these reciprocal axes to the corresponding direct axes.

In the case of the determination of the a axes of hexagonal crystals, this consists of the measurements of the x values of the spots along either one of the two position symmetry lines of the equator photograph for the c axis rotation. Either the long diagonal identity period or the short diagonal identity period along the diamond reciprocal cell may be so measured. The resulting transformation to direct cell axes from one of these reciprocal measurements is indicated in Fig. 5.

In the case of the determination of the c axis by this general method, the following points should be remembered. The equator photograph of any zone containing the basal pinacoid may be used. In rhombohedral crystals, only the orders of (0001) divisible by 3 can appear as reflections due to the rhombohedral centering (Fig. 7), and, if the possible vertical symmetry plane is a glide plane, only orders of (0001) divisible by 6 appear. Missing equatorial spectra also occur in the hexagonal crystals due to space group symmetry operations.

[7] Reference 4, pages 276–283.

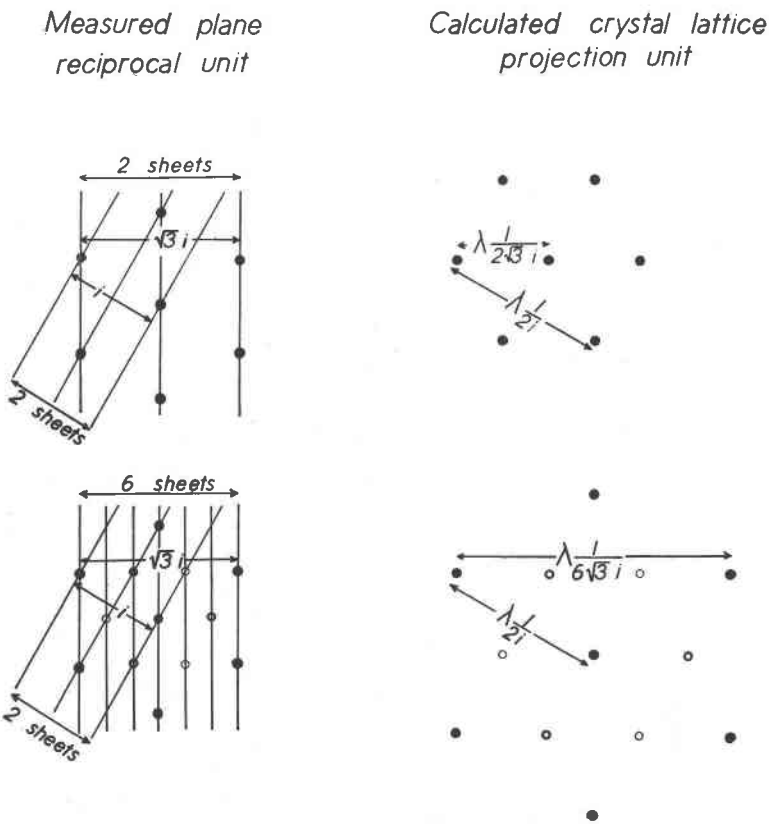

FIG. 5

REFINING OF LATTICE DIMENSIONS

In another place, one of the writers has called attention[8] to the possibility of refining lattice dimensions derived from measurements made on photographs taken with a single crystal, by means of the method which Bradley and Jay[9] applied to powder photographs with great success. The writers give examples of this technique applied to the refining of the lattice dimensions of the Etta tourmaline. Measurements were made of the film equivalent of the identity period along the short diagonal of the reciprocal lattice. These measurements transform to the direct hexagonal axis with the aid of the relation:[8]

[8] Buerger M. J., The *x*-ray determination of lattice constants and axial ratios of crystals belonging to the oblique systems: *Am. Mineral.*, vol. **22**, pp. 424–425, 1937.

[9] Bradley, A. J., and Jay, A. H., A method for deducing accurate values of the lattice spacings from *x*-ray powder photographs taken by the Debye-Scherrer method: *Proc. Phys. Soc.*, vol. **44**, pp. 563–579, 1932.

TABLE 1. COMPUTATION OF APPARENT LENGTH OF THE HEXAGONAL A-AXIS, FOR USE IN PLOTTING FIG. 6

Order	20	20	22	20	18	16	16	14
Radiation	$CuK\alpha_2$	$CuK\alpha_1$	$CuK\beta_1$	$CuK\beta_1$	$CuK\alpha_1+\alpha_2$	$CuK\alpha_1+\alpha_2$	$CuK\beta_1$	$CuK\alpha_1+\alpha_2$
λ	1.54123Å	1.53739Å	1.38935Å	1.38935Å	1.53931Å	1.53931Å	1.38935Å	1.53931Å
Film reading, x_2	159.91 mm.	159.34 mm.	158.18 mm.	145.49 mm.	145.06 mm.	135.40 mm.	129.07 mm.	127.40 mm.
Film reading, x_1	9.17	9.65	10.86	23.72	24.01	33.81	40.26	41.95
$2x(=x_2+x_1)$	150.74	149.69	147.32	121.77	121.05	101.59	88.81	85.45
x	75.37	74.845	73.66	60.885	60.525	50.795	44.405	42.725
$\theta(=x+0.001x)$	75.445°	74.919°	73.733°	60.945°	60.585°	50.845°	44.449°	42.767°
θ	75°27′	74°55′	73°44′	60°57′	60°35′	50°51′	44°27′	42°46′
Log $(n/2)$	1.00000	1.00000	1.04139	1.00000	0.95424	0.90309	0.90309	0.84510
Log λ	0.18786	0.18678	0.14281	0.14281	0.18733	0.18733	0.14281	0.18733
Log $(n/2\ \lambda)$	1.18786	1.18678	1.18420	1.14281	1.14157	1.09042	1.04590	1.03243
Log sin θ	9.98584-10	9.98477-10	9.98226-10	9.94161-10	9.94005-10	9.88958-10	9.84528-10	9.83188-10
Log d	1.20202	1.20201	1.20194	1.20120	1.20152	1.20084	1.20062	1.20055
d	15.922Å	15.922Å	15.920Å	15.892Å	15.903Å	15.880Å	15.872Å	15.867Å
$\cos^2\theta$	0.0631	0.0677	0.0785	0.2355	0.2415	0.401	0.509	0.538

$$A, C = \frac{n\lambda}{2 \sin \theta} = \frac{n\lambda}{2 \sin \left(\frac{x}{2} \cdot \frac{360}{2\pi r_F} \right)}.$$

These calculations are conveniently arranged in tabular form as shown in Table 1. The plotting of the drift of the observed lattice constant

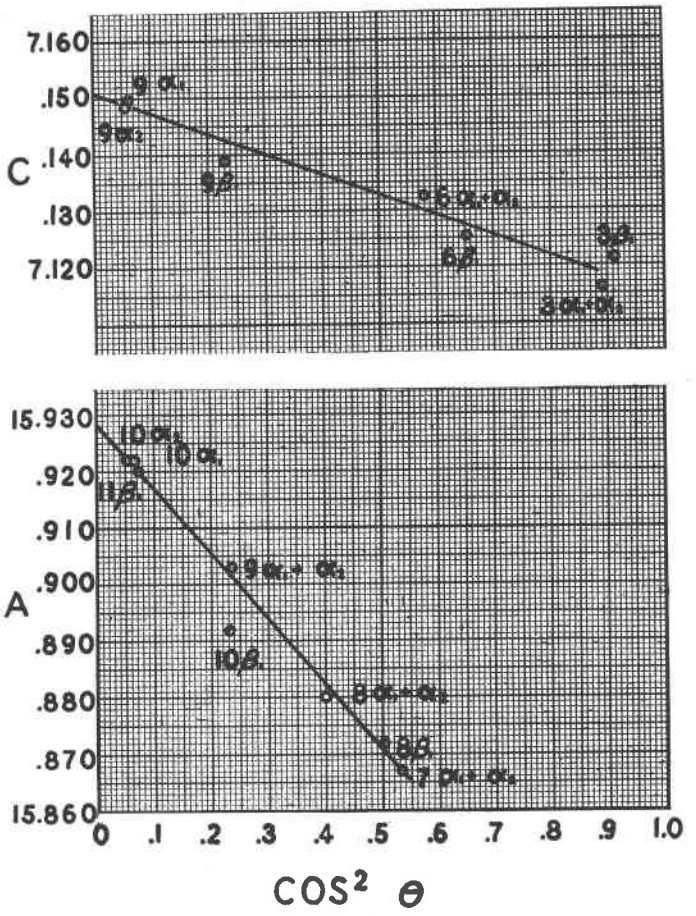

FIG. 6

against the film position of the spot, in the form of $\cos^2 \theta$, is shown in Fig. 6. This procedure leads to the following refined cell dimensions for the Etta tourmaline, referred to a hexagonal frame:

$$A = 15.928\text{Å}$$
$$C = 7.151$$
$$\frac{C}{A} = 0.4490.$$

Transformation from Hexagonal Coordinates to Rhombohedral Coordinates

In Fig. 7 the projection of part of a rhombohedral lattice upon (111) = (0001) and a section along $(10\bar{1}) = (11\bar{2}0)$ are shown. From these it is apparent that a crystal based upon a rhombohedral lattice can be referred to a cell having hexagonal identity periods. If the hexagonal

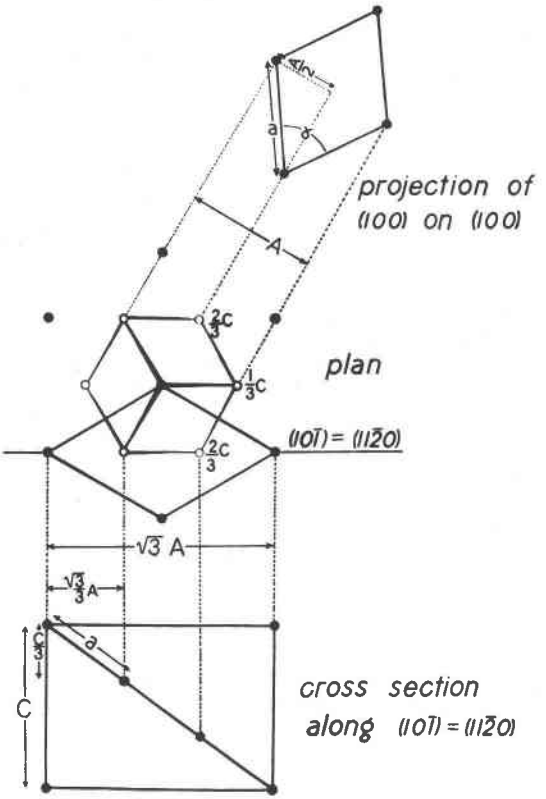

Fig. 7

identity periods are designated A and C, it is evident from Fig. 7 that the rhombohedral identity period is related to it as follows:

$$a^2 = \left(\frac{\sqrt{3}A}{3}\right)^2 + \left(\frac{C}{3}\right)^2$$

from which,

$$a = \tfrac{1}{3}\sqrt{3A^2 + C^2}. \qquad (1)$$

Figure 7 also shows one of the rhombohedral faces of the rhombohedral unit cell projected on a plane parallel with itself. From this projection it

can be seen that the rhombohedral interaxial angle, α, may be derived from the following relation:

$$\sin \frac{\alpha}{2} = \frac{A/2}{a}. \tag{2}$$

Substituting in (2), the value of a given by (1) yields the useful relation:

$$\sin \frac{\alpha}{2} = \frac{6A}{\sqrt{3A^2 + C^2}}. \tag{3}$$

Another form of this relation may be obtained by substituting the value of sin $\alpha/2$ given by (3) in the trigonometric identity:

$$2 \sin^2 \frac{\alpha}{2} = 1 - \cos \alpha. \tag{4}$$

This gives the rhombohedral interaxial angle in a form dependent only on the hexagonal axial ratio, C/A, thus:

$$\alpha = \cos^{-1} \left[\frac{2\left(\frac{C}{A}\right)^2 - 3}{2\left(\frac{C}{A}\right)^2 + 6} \right]. \tag{5}$$

When these transformations have been applied to the hexagonal dimensions of the Etta tourmaline cell, the following rhombohedral cell dimensions result:

$$a = 9.500 \text{ Å}$$
$$\alpha = 66°05'$$

Discussion

While the cell dimensions given here are comparable with those of earlier investigators, the other results differ radically in referring tourmaline to a rhombohedral lattice rather than to a hexagonal lattice. This, of course, completely changes the space group of tourmaline and has a radical effect on any attempt to derive the crystal structure of tourmaline. The writers are continuing this aspect of the investigation.

It is believed that the earlier investigations went astray because their methods (Laue and rotation) were not sufficiently powerful to resolve reflections for a crystal with such a large A axis (about 16 Å). The short wavelengths of tungsten and molybdenum radiation employed contributed to the difficulty of resolving reflections, but it is doubtful whether longer radiation would have helped greatly with the rotation method. The long axis is, however, ideally handled with the equi-inclination Weissenberg method.