

## CRYSTALLOGRAPHY OF HERAPATHITE

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After a century of obscurity, the artificial crystal, herapathite, has lately assumed, by virtue of its extraordinary dichroism, a technical importance hardly second to that of more familiar natural crystalline materials such as quartz and calcite. This situation has arisen through the recent successful preparation of large area transmission polarisers (Polaroid, Herotar, etc.) using herapathite as starting material, by several different processes on both sides of the Atlantic. Under such circumstances the geometrical and optical properties of herapathite deserve more study than they have hitherto received in the literature of crystallography. It is hoped that the present account, while far from definitive, will at least begin to fill this deficiency.

*Composition.* The composition of herapathite has been shown by Jørgensen (1877) and others to be (I)  $4\text{C}\cdot 3\text{SO}_4\cdot 2\text{I}_3\cdot 6\text{H}_2\text{O}$ , where C denotes the quinine molecule  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$ . The crystal can give up at least some of its water without losing its form and optical properties. It is an acid sulfate triiodide of quinine. Jørgensen found several other crystals built up of the components C,  $\text{H}_2\text{SO}_4$ , HI,  $\text{I}_2$ , having crystal forms and optical properties closely similar to those of herapathite. His formulas for three of these herapathitic crystals may be written, for convenience,  $4\text{C}\cdot 3\text{SO}_4\cdot 2\text{I}\cdot \text{I}_n$ , where  $n=5, 6, 7$  (compounds II, III, IV), and for a fourth crystal (VI)  $4\text{C}\cdot 2\text{SO}_4\cdot 4\text{I}_3$ . Jørgensen also found several selenate herapathites having crystal forms and compositions corresponding to the foregoing sulfate herapathites, notably (I) and (III).

Although the crystals examined in the course of the present work were not analysed, there can be no doubt that they belong to Jørgensen's isostructural group and are fairly representative. They are fragile brown plates up to 1 cm. in diameter found in several different herapathite preparations; the latter had been precipitated in a finely divided form about two years previously and left standing under the mother liquor in sealed containers, where they had obviously recrystallised. In addition some smaller green plates, the familiar form of herapathite described in the literature, were also examined.

*Morphology.* The crystal plates belong to the orthorhombic system, the somewhat irregular development of the pyramid faces leaves the symmetry class in doubt. The  $a$ -axis is taken as the plate normal, the  $c$ -axis as the direction in the plate parallel to which light vibrations are strongly absorbed; the plates are sometimes elongated along  $b$ . Light vibrations parallel to the  $a$  and  $b$  axes are freely transmitted.

Lot 1 (brown crystals). The density measured by suspension is 1.645. The axial ratio, averaged from two-circle measurements of four selected crystals measured with reference to the  $b$ -axis, is  $a:b:c=2.202:1:1.268$ . The crystals show the forms  $\{100\}$  (plate face),  $\{110\}$ ,  $\{310\}$ ,  $\{101\}$ ,  $\{201\}$  and  $\{211\}$ . Another preparation shows the form  $\{321\}$  also. Measurements of Lot 1 are summarized in Table 1, and a drawing is shown in Fig. 1.

TABLE 1. HERAPATHITE (LOT 1). TWO-CIRCLE ANGLES  
 $a:b:c=2.2020:1:1.2679$ ;  $r_2:p_2:q_2=0.7887:0.4541:1$

Form	Faces	Measured Limits		Measured Mean		Calculated	
		$\phi_2$	$\rho_2$	$\phi_2$	$\rho_2$	$\phi_2$	$\rho_2$
100	8	—	—	0°00'	90°00'	0°00'	90°00'
110	6	—	24°19'–24°37'	0 00	24 28	0 00	24 25½
310	2	—	53 12–53 18	0 00	53 15	0 00	53 43
101	12	59°16'–60°18'	—	60 02	90 00	60 04	90 00
201	4	40 10–41 31	—	40 49	90 00	40 58	90 00
211	8	40 40–41 42½	49 49–50 37	41 06½	50 24	40 58	50 16
(321)	2	29 40–32 02	—	30 51	38 55	30 04	38 12½

Lot 2 (brown crystals). Three crystals measured in normal position yield the axial ratio 2.251:1:1.268. Forms observed are  $\{100\}$ ,  $\{110\}$ ,  $\{210\}$ ,  $\{101\}$ ,  $\{211\}$ ; the measurements are summarised in Table 2.

TABLE 2. HERAPATHITE (LOT 2): TWO-CIRCLE ANGLES  
 $a:b:c=2.2515:1:1.2679$ ;  $p_0:q_0:r_0=0.5631:1.2679:1$

Form	Faces	Measured Limits		Measured Mean		Calculated	
		$\phi$	$\rho$	$\phi$	$\rho$	$\phi$	$\rho$
100	6	—	—	90 00'	90 00'	90°00'	90°00'
110	9	22°50'–24°10'	—	23 35	90 00	23 57	90 00
310	9	52 49–53 46	—	53 21	90 00	53 07	90 00
101	5	—	29°15'–29°33'	90 00	29 23	90 00	29 23
211	7	41 20–42 39	59 08–59 47	41 52	59 21	41 37	59 28½

Lot 3 (small green crystals). On one plate it was possible to make approximate settings on the extremely narrow edges of  $\{110\}$  (4 faces) and  $\{101\}$  (2 faces). These give the average values  $\phi(110)=23°53'$ ,  $\rho(101)=29°19'$ , which by chance agree well with values found for Lot 2 (table 2).

Lot 4 (small green crystals). The density by suspension is 1.700; this figure is somewhat higher than that given for Lot 1, and very much lower than 1.895 as given by Herapath (1855). The corners of the rectangular plates are cut off by two oblique edges (Fig. 2). For comparison with the

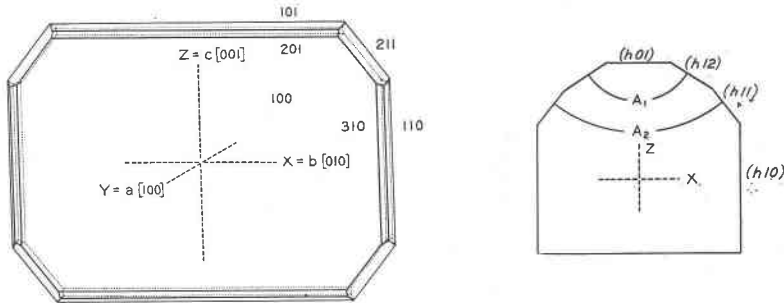


FIG. 1 (left). Herapathite, faces and optical orientation.

FIG. 2 (right). Herapathite, edge angles and optical orientation.

measurements of Herapath, and of Jørgensen, I measured the angles  $A_1$  and  $A_2$  with a petrographic microscope. If the edges are taken to represent intersections of faces  $(h11)$  and  $(h12)$  with  $(100)$ , satisfactory agreement is found not only with the earlier work, but also with the present goniometric measurements.

	H.	J.	W.	calc.
$A_1 (h12)$	115°	116°	116.4°	115.3°
$A_2 (h11)$	75	77	77.5	76.5

The calculated values of these two angles are here based on  $b:c = 1:1.268$ .

It will be noted that while  $(h11)$  may be the same as  $(211)$  given above, no face corresponding to  $(h12)$  was found with the goniometer.

With reference to the optical orientation, the direction designated as the "plane of polarisation" of the incident light by Herapath and Jørgensen must be taken as perpendicular to the direction now conventionally denoted by the "vibration direction" of the light. The orientation stated by Groth (1907) is incorrect.

*Optics.* A complete optical investigation of the herapathite crystal would define its absorption, its reflection and its refraction for a light ray, polarised in any azimuth, propagated in any direction relative to the crystallographic axes, and incident on any section of the crystal. Obviously this would be a formidable task.

As previously stated, the absorption for light vibrating parallel to  $c$  is enormously greater than that for light vibrating parallel to  $a$  or  $b$ ; indeed, in the basal section the latter two axes cannot be distinguished in their absorption. The absorption ellipsoid is thus in effect a rotation

surface greatly elongated along its axis which coincides with the *c*-axis of the crystal. Data on the double absorption of herapathite, in relative measure, for the visible spectrum have recently been published by Haase (1936).

The reflection and absorption of herapathite crystals were described in an early paper by Haidinger (1853).

I measured the principal refractive indices by the immersion method in Na light as:  $\alpha \parallel b = 1.608$ ,  $\beta \parallel a = 1.625$ . It will be possible to measure  $\gamma$  directly by transmission only with far red or infra red light. Thin basal sections in convergent light show a typical positive acute bisectrix figure, at least for rays of not too great obliquity. The optic axes lie in the (100) plane, the angle between them is small with  $2V$  estimated at about  $10^\circ$ , the dispersion is moderate with red  $>$  green. Blue green light of  $\lambda$  about  $490 \text{ m}\mu$  is already quite strongly absorbed, while  $530 \text{ m}\mu$  is readily transmitted.

*X-ray Measurements.* The absolute axial lengths of crystals of Lot 1 were measured approximately from layer line separations of rotation photographs (CuK) as follows:  $a_0 : b_0 : c_0 = 33.30 : 15.15 : 19.24 \text{ AU} = 2.198 : 1 : 1.270$ , in agreement with the goniometric values.

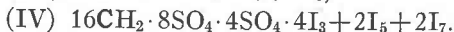
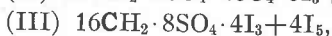
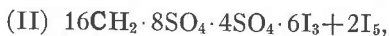
From these axes the molecular weight is calculated as follows:

$$\begin{aligned} V &= abc = 9720 \text{ AU}^3 \\ M &= DV/Z = 2428, \text{ based on } D = 1.645, Z = 4 \\ M &= 2355 \text{ for (I) } 4\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot 3\text{H}_2\text{SO}_4 \cdot 2\text{HI}_3 \\ &\text{or } 2463 \text{ for the same formula plus } 6\text{H}_2\text{O}. \end{aligned}$$

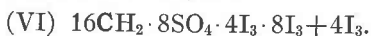
The unit cell of herapathite is an unusually large one. In accord with the orthorhombic symmetry the contents are to be distributed over 2, 4, 8 and 16-fold points; for example



Jørgensen's isostructural crystals might than have some such distributions as:



The last crystal has an excess of four structural units (triiodide ions) over the first four, thus:



Alternative distributions can be easily formulated, the ones given are purely for the sake of illustration. They serve to show that the cell volume found above is large enough so that all the iodine atoms in the several crystals, assuming that they all have the same unit cell, can be present in the form of polyiodide ions of the general formula  $(\text{I}_{2n+1})^-$ .

The unusual optical properties of this isostructural group of crystals and of other strongly dichroic crystals containing iodine may be supposed to be due, first to a linear configuration of the polyiodide ions  $(I_{2n+1})^-$ , second to the orientation of the axes of all these polyiodide ions parallel to the  $c$ -axis of the crystal. It should prove possible to test this supposition by an analysis of  $x$ -ray diffraction data.

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