THE SPACE-LATTICE AND OPTICAL ORIENTATION OF CHALCANTHITE (CuSO$_4$·5H$_2$O): AN ILLUSTRATION OF THE USE OF THE WEISSENBERG X-RAY GONIOMETER IN THE TRICLINIC SYSTEM[1]

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The geometrical crystallography of chalcanthite, CuSO$_4$·5H$_2$O, has been accurately determined by Tutton and by Barker. This substance is triclinic and thus the following discussion of x-ray measurements made by the present authors on an artificial crystal of chalcanthite will serve to illustrate the application of the Weissenberg x-ray goniometer in crystallographic measurements of triclinic substances, and also the relation of the measurements made with the x-ray goniometer to those made with the reflection goniometer.

TABLE 1.
LINEAR GEOMETRICAL ELEMENTS OF COPPER SULPHATE PENTAHYDRATE.

a	b	c	α	β	γ	
0.5715	1	0.5575	82°16′	107°26′	102°40′	Tutton
0.5721	1	0.5554	82°05′	107°08′	102°41′	Barker
0.563	1	0.546	—	—	—	Gossner & Brückl

The geometrical elements of Tutton[2] and of Barker[3] are given in Table 1 together with the axial ratio of Gossner and Brückl[4] obtained by x-ray measurements in combination with the axial angles of Barker. The measurements from which the axial ratio of Tutton was derived are recorded in his classical study of the crystals of copper sulphate pentahydrate. Barker's measurements on which his elements are based have not been published. The third line gives the axial ratio as calculated by Gossner and Brückl from their spacing measurements: $a_0 = 6.07$; $b_0 = 10.78$; $c_0 = 5.89$.

The orientation of Tutton and Barker is not entirely conventional, since the base slopes downward to the left, but will be re-

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[1] Contribution to the Rinne Festschrift.

[2] Tutton, A. E. H., Crystallography and Practical Crystal Measurement, *London*, 1922, vol. **1**, pp. 282 ff.

[3] Groth, P., Chemische Krystallographie, *Leipzig*, 1908, Teil **2**, S. 419.

[4] Gossner, B. and Brückl, K., *Zeit. f. Krist.*, **69**, 422. 1929.

tained in this paper in order that comparison of our results may be made with those of Tutton and of Barker. Tutton's choice of the principal or axial directions (as contrasted with his choice of positive and negative directions along the axes) is, however, most felicitous since the interplanar spacings of the three planes chosen as pinacoids by him are now found to be the greatest, second greatest, and third greatest, respectively, of any three non-tautozonal planes in the crystal; furthermore, in the three zones between the pinacoids the unit prism, (110), and unit domes, (101) and (011), have the greatest spacings except the pinacoids themselves.

Unit Cell Dimensions of Copper Sulphate Pentahydrate

The crystallographic habit of copper sulphate pentahydrate permits an easy orientation of one zone, the axis of which has usually been taken as the c-axis. The crystal was mounted on the Weissenberg goniometer for rotation around this axis and, as will be shown in the sequel, a complete set of crystallographic elements was determined from purely röntgenographic measurements without changing the orientation of the crystal.

In order to obtain the greatest possible accuracy, soft x-radiation was used, in this case Cr-K-radiation, the wave length of which is $\lambda = 2.285$ Å.

(1) An ordinary rotation photograph around the c-axis was produced and from the separation of the layer-lines the spacing along this axis was found to be $c_0 = 5.95$ Å.

(2) One Weissenberg photograph of the first layer-line together with the rotation photograph would be sufficient to determine all the crystallographic elements as well as the absolute dimensions of the unit cell. A Weissenberg photograph of the equator was also taken, however, in order to obtain slightly more accurate values of three of the elements. From it the interplanar spacings normal to 010 and 100 were accurately determined from the higher order reflections of these pinacoids to be:

$$d_{100} = 5.724 \text{ Å}; \quad d_{010} = 10.385 \text{ Å}.$$

Also the crystallographic angle, ν (V. Goldschmidt's designation), which corresponds to the angle, γ^*, in the reciprocal lattice, was determined graphically from this film with the following result:

$$\nu = \gamma^* = 79° \; 15'.$$

(3) From a Weissenberg photograph of the first layer-line the other two crystallographic angles, λ and μ (V. Goldschmidt's designations), corresponding to the angles, α^* and β^*, respectively, in the reciprocal lattice were determined graphically with the use of the construction of Schneider[5] with the following results:

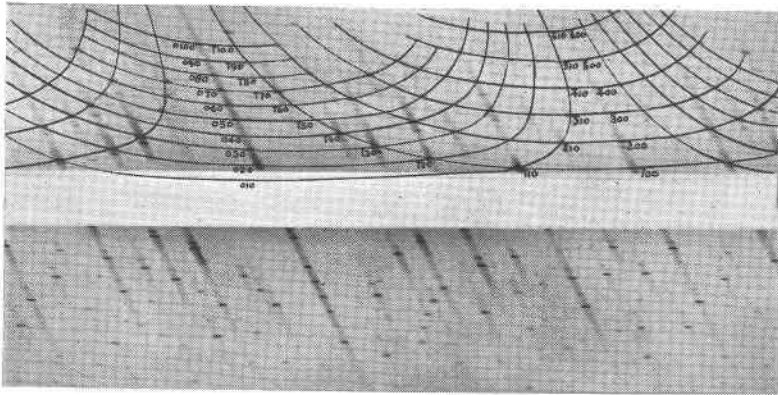$$\lambda = \alpha^* = 94° \ 12'; \quad \mu = \beta^* = 74° \ 00'.$$

Fig. 1

Example of a Weissenberg photograph of a triclinic crystal: the equator line of chalcanthite (Mo-K-radiation). Only the set of curves for the α-spots has been drawn; a similar set of curves could be passed through the β-spots but this set would yield no new information.

(Note: This photograph taken with Mo-radiation was not used in the determination of the reciprocal lattice or crystallographic elements, for which purpose a photograph with Cr-radiation was taken; the photograph with the Mo-radiation of course contains more diffraction spots than that with Cr-radiation and is therefore more suitable as an illustration of a Weissenberg photograph of a triclinic crystal.)

It may be noted here that the graphical construction of Schneider leads directly to a determination of the elements of the reciprocal lattice, based on the x-ray measurements. The best numerical values of the reciprocal lattice were obtained, however, from the planar spacings, d_{100} and d_{010}, and the spacing along the rotation axis, c_0, by simple calculations, and are as follows:

$$a^* = 3.992; \quad b^* = 2.200; \quad c^* = 4.037.$$

Angles α^*, β^*, and γ^* as above. Since the unit parallelepiped of

[5] Schneider, W., *Zeit. f. Krist.*, **69**, 41, 1928.

the reciprocal lattice, which is drawn in Fig. 2, is similar in shape and relative dimensions to the "Polarform" of V. Goldschmidt (α^*, β^*, γ^* correspond to λ, μ, ν, respectively, and a^*, b^*, c^* are proportional to p_0, q_0, $r_0(=1)$, see preceding paper by Tunell) it is obvious that the polar elements can be derived directly from the reciprocal lattice.
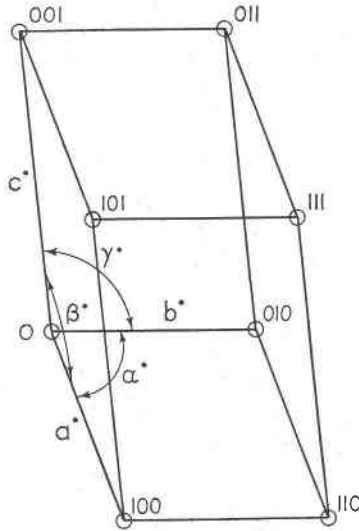

FIG. 2

Reciprocal lattice of chalcanthite ($CuSO_4 \cdot 5H_2O$). O is the origin of the reciprocal lattice.

(Note: The unit parallelepiped of the reciprocal lattice may be considered identical with the "Polarform" of Victor Goldschmidt if the scales of both be properly chosen.)

From the linear elements of $CuSO_4 \cdot 5H_2O$ of Tutton and from those of Barker the polar elements can also be calculated according to well-known crystallographic equations.[6] These calculations have been carried out and the following table gives a comparison of the three sets of polar elements of copper sulphate pentahydrate de-

[6] Goldschmidt, V., Index der Krystallformen der Mineralien, Bd. I, S. 78, 1886; Palache, C., *Am. Mineral.*, **5**, 188–189, 1920.

It should be noted that V. Goldschmidt uses the symbols, a_0, b_0, c_0, in these formulae in the sense of axial lengths referred to c_0 as unity, and *not* in the sense of the absolute lengths of the edges of the unit cell, as is customary among x-ray crystallographers; Palache gives the formulae in terms of the ordinary axial ratio, $a:b:c$, and axial angles, α, β, γ.

rived from Tutton's goniometrical measurements, from Barker's goniometrical measurements, and from purely röntgenographic measurements in the present investigation.

TABLE 2.
POLAR ELEMENTS OF COPPER SULPHATE PENTAHYDRATE.

	Tutton (Reflection goniometer)	Barker (Reflection goniometer)	Barth & Tunell (X-ray goniometer)
p_0	0.99074	0.98561	0.98885
q_0	0.54516	0.54403	0.54503
r_0	1	1	1
λ	94°15'	94°30'	94°12'
μ	73°47'	74°07'	74°00'
ν	79°05'	79°06'	79°15'

It may be seen that the accuracy of the Weissenberg method is quite satisfactory. It may also be stated that slightly better values could be obtained by this method if the crystal were rotated around the other two crystallographic axes as well as the c-axis. It is believed that greater accuracy than that obtained with the Weissenberg method can be secured with the reflection goniometer if the crystal faces are of a high degree of excellence, but not if the faces are dull, striated, or otherwise imperfect.

The crystals of copper sulphate pentahydrate used by Tutton in his classic investigation were of a very high degree of excellence and his angles are probably slightly more accurate than those obtained from the x-ray photographs. It is therefore probable that the most accurate values of the unit cell dimensions of $CuSO_4 \cdot 5H_2O$ are those obtained by combining Tutton's angles, α, β, γ, with our elements, a^*, b^*, c_0. The values for the unit cell thus obtained are:

$a_0 = 6.110 \cdot 10^{-8}$ cm.; $b_0 = 10.673 \cdot 10^{-8}$ cm.; $c_0 = 5.95 \cdot 10^{-8}$ cm.; $\alpha = 82° 16'$; $\beta = 107° 26'$; $\gamma = 102° 40'$.

These values lead to the axial ratio:

$a:b:c = 0.5725:1:0.5575$,

which differs only slightly from that of Tutton given in Table 1.

OPTICAL ORIENTATION OF COPPER SULPHATE PENTAHYDRATE

Although it is such a common substance there is no general agreement as to the optical orientation of copper sulphate pentahydrate.

The optic axial angle was measured by Lavenir[7] to be $(-)2V$ = 56° 02′, a value which is in close agreement with the one calculated[8] from the indices measured by Kohlrausch[9] and by Lavenir.[10]

The position of the optical indicatrix has been surveyed by Pape,[11] Lavenir,[12] Wulff,[13] Weber,[14] and Mélon,[15] with conflicting results.

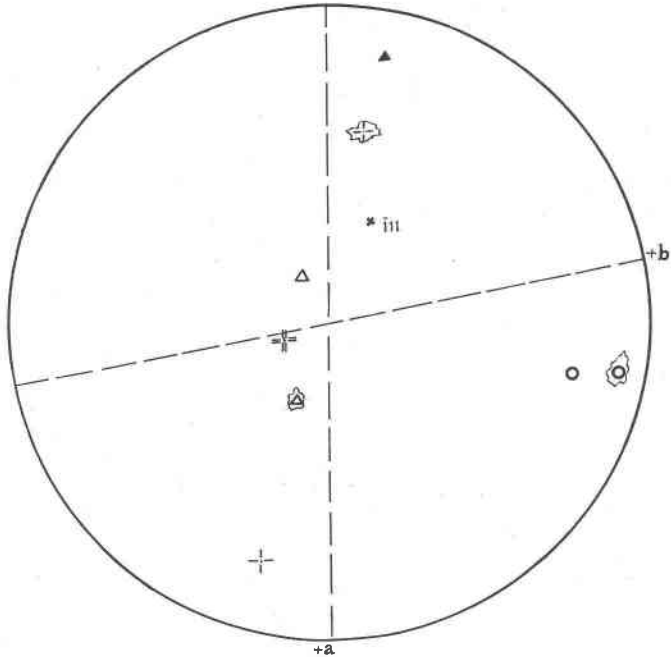Fig. 3

Stereographic projection showing the supposed optical orientation of copper sulphate pentahydrate according to Pape, Weber, and Mélon.

	α	β	γ
Pape	○	-⊢	△
Weber	⊙	⊕	⬡
Mélon	○	⊫	▲

[7] Lavenir, A., *Bull. Soc. Française de Min.*, **14**, 100, 1891.

[8] Cf. Tunell, G. and Morey, G. W., *Am. Mineral.*, **17**, 406, 1932. (The value of 2V calculated by Lavenir is slightly inaccurate.)

[9] *Wiedemann's Ann. d. Physik und Chemie*, **4**, 30, 1878.

[10] *Op. cit.*

[11] Pape, C., *Pogg. Ann. d. Physik und Chemie*, Ergänzungsband **6**, 35, 1874.

The data given by Pape, Weber, and Mélon are reproduced in the stereographic projection of Fig. 3. The data of Lavenir have not been included, for the presentation of his observations is such that a unique interpretation of his data is impossible. It is not clear
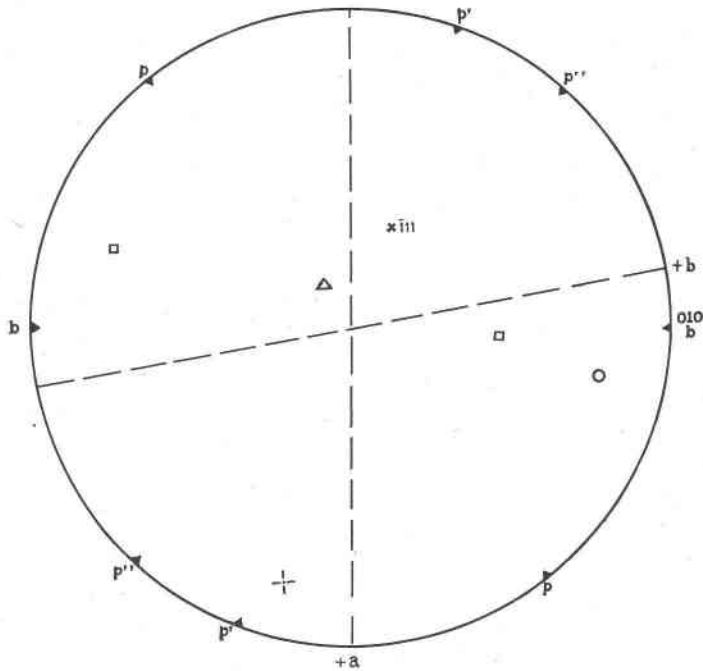

Fig. 4

Stereographic projection of the optical orientation of copper sulphate penta-hydrate as determined by the present authors.

$\circ = \alpha, \dotplus = \beta, \triangle = \gamma, \square = $ optic axis.

$2V_\alpha = 56°$, $c:\gamma = 18°$ in a plane forming $33°$ with 010, and $c:\alpha = 76°$ in a plane forming $79°$ with 010. (Since there are two planes forming the same angle with (010) the projection serves to fix uniquely the directions of the axes of the optical ellipsoid.)

The orientation and the letters assigned to the faces are the same as those of Tutton.

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[12] *Op. cit.*

[13] Wulff, G., in Groth's "Chemische Krystallographie," *Leipzig*, 1908, Teil 2, S. 420.

[14] Weber, L., *Mitt. Naturf. Gesellsch. i. Freiburg* (Schweiz) 4, 103, 1921.

[15] Mélon, J., *Bull. Soc. Française de Min.*, 47, 141, 1924.

whether Wulff's results are based on original observations or are recalculations of Pape's findings, with which they coincide.

The wide discrepancies shown in the stereographic projection of the data in the literature make a reinvestigation of the optical orientation of this substance imperative. The use of a Fedorov stage offers a simple and rapid method of determining the optical orientation of any triclinic crystal. Higher accuracy can be obtained by other methods but the accuracy of the measurements with the Fedorov stage is amply sufficient for most purposes.

Small, well faceted crystals of copper sulphate pentahydrate obtained by evaporation of a saturated solution were imbedded in canada balsam on microscope slides for optical study. The faces of the crystals were easily identified with the aid of the Fedorov stage. The average of several measurements of interfacial angles and extinction angles established the orientation represented in the second stereographic projection (Fig. 4).

A comparison of Figs. 3 and 4 shows that the measurements of the present authors are in good agreement with those of Pape; they also are in agreement with one of the four possible interpretations of Lavenir's data.

Summary

The crystallographic elements of the triclinic substance, chalcanthite ($CuSO_4 \cdot 5H_2O$) have been determined by purely röntgenographic measurements with a Weissenberg goniometer (see Table 2).

The most accurate dimensions of the unit cell with the largest possible spacings in the directions normal to the three pinacoids are:

$$a_0 = 6.110 \text{ Å}; \qquad b_0 = 10.673 \text{ Å}; \qquad c_0 = 5.95 \text{ Å};$$
$$\alpha = 82° \ 16'; \qquad \beta = 107° \ 26'; \qquad \gamma = 102° \ 40'.$$

This unit cell corresponds to the choice of crystallographic axes made by Tutton and Barker, whose orientation therefore has been adopted.

The optical orientation of chalcanthite has been redetermined with a Fedorov stage and the results are represented in a stereographic projection (Fig. 4). They are in close agreement with the results of Pape.