## CRYSTALLOGRAPHY OF TSUMEBITE

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## Introduction

The mineral tsumebite, found only at Tsumeb, Southwest Africa, was described by Busz ${ }^{1}$ in 1912 as monoclinic. In the same year Rosicky ${ }^{2}$ described similar material from Tsumeb, under the name of preslite, as orthorhombic. Before his paper was published his attention was directed to the article by Busz, just out, and he added a note to his own, suggesting the identity of the two minerals, as the analyses agreed closely, but adhering to his interpretation of the symmetry. There is no doubt of the identity, but the translation from one setting to the other, worked out by him, is wrong.

The Harvard Mineral Collections contain two specimens of tsumebite. On both the mineral forms tiny groups of lustrous emerald-green crystals implanted on smithsonite, as originally described. Crystals of the tsumebite have been measured by the writer, who agrees with Busz in regarding them as monoclinic and as invariably twinned. No untwinned crystals or simple twinned pairs were found on the two specimens, only "groups (of twins) intergrown or tangled with one another" (Busz). In some the crystals are in sub-parallel position, in others "tangled" as in tufts of felt. Few groups are more than 2 mm . across and many are so small that mounting them for measurement is difficult, but all are twinned.

## Character of the Crystals

Both previous authors understated the difficulty of measuring the crystal angles, although some faces are smooth and bright and give fairly sharp signals. Much trouble is due to intergrowth of crystals in groups, making it difficult to decide from which one the signals are reflected, as faces on different crystals may be so nearly parallel as to give close double signals. Moreover, on many groups parts of their surfaces that appear under the bench microscope with low power as dull crystal faces prove, when examined on the goniometer with higher magnification, to be irregular or curved splintery areas that reflect no definite signals and cannot be recognized as crystal faces. Scattered about on the groups, in the rough patches and also on edges and corners of faces, are small bright facets which gave good signals. Their distribution on the groups bears no relation to their crystallographic positions and none of them can be
${ }^{1}$ Busz, Karl, Tsumebite, ein neues Blei-Kupfer-Phosphat von Otavi, Deutsch Süd-West-Afrika: Deutsch. Naturf. u. Årtze in Miunster, Versammlung, vol. 84, p. 162, 1912.
${ }^{2}$ Rosický, V., Preslit, ein neues Mineral von Tsumeb in Deutsch Südwestafrika: Zeits. Krist., vol. 51, p. 521, 1912.
identified at sight. When their angular relations are plotted, they are found to occupy the poles of crystal forms known on tsumebite and, as they have been seen and measured repeatedly, there seems to be no reason for not regarding them as valid crystal faces. Their apparently irregular distribution is due to their belonging to different ones of the intergrown crystals.

A uniform setting of such crystals for measurement is necessary as without it the crystals cannot be interpreted. The face called by the writer $\{100\}$ is a narrow face that usually gives a good signal and is flanked on one or both sides by the unit prism, recognizable by its luster and signals. Every group of crystals bears this key combination in one


Fig. 1. Plan and clinographic projection of the writer's ideal of an untwinned crystal of tsumebite, showing the commoner forms.
Fig. 2. Clinographic projection of a twinned crystal of tsumebite of the " Y " type, considerably idealized by being drawn as complete.
or more places (Figs. 1 and 2) and each place where it shows is the front coign of a crystal that may be set up on a two-circle goniometer either with the narrow face as the pole or with the combination as the prism one.
This combination includes no terminal faces and so the top of the crystal can not be determined until all the angles have been measured and not even then unless certain needed terminal faces are present and measured.

Some relatively simple groups show the mode of twinning, but not until all the groups had been measured and plotted and their projections carefully analyzed was the true morphology of the crystals discovered. Until then it was not possible to differentiate on a projection the faces belonging respectively to the several crystals of a group or, even though the twin law was known, to distinguish all the twinned face poles from the untwinned ones. The pole of the twinning axis lies at the intersection of four of the zones developed on the crystals and all forms in those zones still lie in the same zones on the projection when twinned (Fig. 3).

Moreover, no one crystal shows faces of all the forms found on tsumebite and most crystals are so intergrown with others that it is impossible by inspection to decide which faces belong to which crystal. The net result of these complexities is an apparently unsymmetrical distribution of face poles on the projections of nearly all the groups measured that is difficult to interpret and to which the former misconceptions of the morphology of the crystals were mainly due, especially as their authors had no sure criteria for distinguishing twinned from untwinned faces or the top of the crystal from the bottom.

## Method of Analysis of the Angle Measured

A number of crystal groups detached from the specimens were examined on the goniometer. Some were unsuitable for measurement but all that could be set up in the uniform position were measured and plotted. The measured angles must be plotted on a stereographic projection so that interfacial angles may be compared directly. Such a projection was made of each group measured, as well as a composite projection of all the groups. On those of the more complex groups the face poles are scattered apparently at random and at first sight their interpretation seems hopeless. Some projections defied interpretation and on some the angles were too poor for use, but about 30 had faces that gave usable readings.

All the angles were measured on a two-circle goniometer, so some of them are interfacial and some are interzonal. Several hundred measurements from more than 40 angles were plotted on the projections that
could be used and more than 200 of these measurements were found to be of angles between identifiable faces or zones. They were analyzed for consistency and approximate elements were computed from ten selected interfacial and four interzonal angles. It then became evident that, because of the mode of twinning and the peculiar morphology of the crystals, the elements could be completely determined from the interfacial angle $a-m$ and the interzonal angle $d-a-u$. As there were more and generally better measurements of those two angles than of any others, a final set of elements and angle table were computed from them.

There were twelve forms found on the crystals: the front pinacoid, five prisms, three orthodomes, two clinodomes, and one pyramid. In the position chosen there is no base and no side pinacoid. Of the forms found, seven are common, four are rare but certain, and one is uncertain. All but two were found in both normal and twin positions. The twin law is simple, the twin plane (not an observed form) being either ( $\overline{122}$ ) or (122) and trillings were seen twinned on both planes (Figs. 3 and 4). The twin plane passes through opposite faces of the unit prism and nearly coincides with the zone [112]. The crystals thus closely simulate isometric forms in their angles, but the face distribution is clearly monoclinic.

Table 1. Frequency and Equivalence of Forms.

| Form | Number of Times Identified |  |  | Busz | Rosický |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Normal | Twinned | Total |  |  |
| $a(100)$ | 35 | 10 | 45 | ${ }_{o}(101)$ | $d(101)$ |
| $k(140)$ | 3 | 3 | 6 | ....... | ....... |
| $l(120)$ | 1 | 2 | 3 |  | $n(121)$ ? |
| $m(110)$ | 77 | 23 | 100 | $p$ (111) | $p(111)$ in part $\dagger$ |
| $n(320)$ | 5 | 0 | 5 | . | ...... |
| $o(210)^{*}$ | 0 | 2 | 2 | ....... | . .1. . |
| $d(101)$ | 16 | 3 | 19 | $a(100)$ | c(001) |
| $e(201)$ | 3 | 2 | 5 |  | $e^{\prime}(201)$ |
| $f(\overline{\mathrm{~T}} 04)$ | 17 | 8 | 25 | $d(101)$ | ...... |
| $u(011)$ | 36 | 31 | 67 | $n(221)$ | ...... |
| $v(021)$ | 4 | 8 | 12 | ...... | $\ldots .$. |
| $r(241)$ | 12 | 12 | 24 | . | ...... |

* Uncertain.
$\dagger$ Only four of the eight faces of the unit pyramid of Rosicky are equivalent to the unit prism of the writer.


## Comparison with Previous Lists

Busz listed only seven forms on tsumebite and Rosický only four on preslite. Therefore, and also because each author has used a different
setting, not all the forms in the three lists can be correlated (Table 1). Comparison of the drawings, however, shows the equivalence of the dominant forms that govern the crystal habit. The forms $o, a, d$, and $p$ of Busz are easily recognized as equivalent, respectively, to the new forms $a, d, f$, and $m$; and the $n$ of Busz seems to be the new $u$. The statement of Busz that his zone $d-s-n$ is deeply striated parallel to the zone-axis shows that it must be the zone of oscillatory combination of the writer's $f$ and $u$ (Fig. 5). No forms corresponding to the $r$ and $s$ of Busz have been seen.

Correlation with Rosicky's forms is not so easy, as his figures are drawn with three planes of symmetry in the belief that the crystals were orthorhombic. Of the many crystals examined by the writer not one showed a plane of symmetry parallel to the large face, taken as the base by Rosicky. He seems not to have distinguished between some faces of his "form" $p$ and the zones of oscillatory combination, which lie nearly, but not actually, in vertical zones with the real faces of his $p$, which is clearly the same as the new $m$. Rosicky's $c, d$, and $e$ are the same, respectively, as the new $d, a$, and $f^{\prime}$.

The other forms found by the writer were not recorded by the earlier authors; even the pyramid $\boldsymbol{r}$ (241), which is one of the common forms in both normal and twin position, seems to have been overlooked or else taken for a face of some other form.

The setting here adopted seems justified because the zone taken as the prism zone not only includes more forms than any other on the crystals, but is the only one normal to the symmetry plane that will serve satisfactorily as the prism zone. Also the zone taken as the clinodome zone is the only one near the axis of the prism zone. Finally, the new setting gives simple rational indices for the pole of the twinning axis.

The translation from the setting of Busz to the new one is effected by interchanging the front pinacoid and the unit orthodome after reversing the crystal about the (former) vertical axis (Table 1). The transformation of the elements is more complex because both the $a$ and $c$ axes are changed. The upper half of one of Rosicky's supposed orthorhombic crystals can be translated to the new setting by rotation on the $b$ axis so that his (101) becomes (100). No such translation of the lower half is possible as the crystals are not orthorhombic and the lower faces of his pyramids are in reality twinned faces of other forms not listed by him. The translation suggested by Rosický from the setting of Busz to his own was based on an erroneous premise and so is not possible.


Fig. 3. Gnomonic projection of tsumebite, showing also the poles of the commoner forms in twinned position.

The poles of forms in normal position are shown by full black circles, those of forms in twinned position by open circles. The more important zones in twinned position are shown bv dotted lines.

## Crystal Constants

Tsumebite is definitely monoclinic and the elements computed from the new angle measurements to fit the new setting are as follows: $a=0.65462, c=q_{0}{ }^{\prime}=0.67451, p_{0}{ }^{\prime}=1.03338, e^{\prime}=0.07642, \mu=85^{\circ} 37^{\prime} 48^{\prime \prime}$.

The angle table below differs in form from that used at Harvard in that the angles from the several forms to the basal and side pinacoids are omitted, as those forms are not found on the mineral. Instead the angles $(M)$ to the nearest face of the unit prism are given, as that is the most conspicuous and easily recognized form on the crystals and lies in three zones besides the prism zone. As all the crystals are twinned and as there is no way of distinguishing most of the twinned faces except by their angles to others, the commoner forms in twin position are included
in the table. The coordinates of the twinning plane are also given for convenience.

Table 2.-Angles of Tsumebite

|  | Form | $\phi$ | $p$ | A | M | $x^{\prime}$ | $y^{\prime}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| In normal position | a 100 | $90^{\circ} 00^{\prime}$ | $90^{\circ} 00^{\prime}$ | $\ldots$ | $33^{\circ} 08^{\prime}$ |  |  |
|  | $k \quad 140$ | 2057 | 9000 | $6902 \frac{1}{2}$ | $3554 \frac{1}{2}$ |  |  |
|  | $l \quad 120$ | 3727 | 9000 | 5233 | 1925 |  |  |
|  | $m \quad 110$ | 5652 | 9000 | 3308 |  |  |  |
|  | $n \quad 320$ | 6629 | 9000 | 2331 | 937 |  |  |
|  | - 210 | $7155 \frac{1}{2}$ | 9000 | $1804 \frac{1}{2}$ | $1503 \frac{1}{2}$ |  |  |
|  | d 101 | 9000 | $4758 \frac{1}{2}$ | $4201 \frac{1}{2}$ | 5132 | 1.1098 | 0.00 |
|  | e 201 | 9000 | 6459 | 2501 | 4038 | 2.1432 | 0.00 |
|  | $f \quad \overline{\mathbf{I}} 04$ | -9000 | $1018 \frac{1}{2}$ | 79 41䨐 | 8123 | -0.1819 | 0.00 |
|  | $u \quad 011$ | 628 | 3410 | $8622 \frac{1}{2}$ | $6901 \frac{1}{2}$ | 0.0764 | 0.6745 |
|  | ข 021 | $314 \frac{1}{2}$ | 53 292 | $8723 \frac{1}{2}$ | 6132 | 0.0764 | 1.3490 |
|  | $r \quad 241$ | $3827 \frac{1}{2}$ | 7349 | 5319 | 2419 | 2.1432 | 2.6980 |
| In twinned position | $\begin{array}{ll}a^{\prime} & 100\end{array}$ | 6447 | $5743 \frac{1}{2}$ | 4006 | 3308 | 1.4322 | 0.6745 |
|  | ${ }^{k} \quad 140$ | -13154 | 5502 | $5224 \frac{1}{2}$ | $3554 \frac{1}{2}$ | -1.0644 | -0.9551 |
|  | $m^{\prime}$ I10 | 8243 | 2634 | 6340 | 6616 | 0.4960 | 0.0634 |
|  | $\begin{array}{ll}u & 011\end{array}$ | - $5941 \frac{1}{2}$ | 5312 | $4616 \frac{1}{2}$ | 3654 | -1.1539 | 0.6745 |
|  | $v \quad 021$ | -80 121 | 4037 | $5005 \frac{1}{2}$ | $5317 \frac{1}{2}$ | -0.8452 | 0.1459 |
|  | $r \quad 241$ | $-11017 \frac{1}{2}$ | 6910 | 2846 | 2419 | -2.4651 | -0.9015 |
|  | $f \quad 104$ | -24 05 | 7214 | 6708 | $3648 \frac{1}{2}$ | -1.2734 | 2.8491 |
|  | $d^{\prime}{ }^{\prime} \quad \overline{101}$ | 10650 | $7516 \frac{1}{2}$ | $2213 \frac{1}{2}$ | $2149 \frac{1}{2}$ | 3.6420 | -1.1020 |
|  | $e^{\prime} \quad \overline{201}$ | 9119 | 6648 | 2314 | $3838 \frac{1}{2}$ | 2.3329 | -0.0536 |
|  | $u^{\prime \prime \prime} 01 \overline{1}$ | 16216 | $7141 \frac{1}{2}$ | $7311 \frac{1}{2}$ | $4234 \frac{1}{2}$ | 0.9205 | -2.8723 |
|  | $v^{\prime \prime \prime \prime} 02 \overline{1}$ | 17538 | $5620 \frac{1}{2}$ | $8654 \frac{1}{2}$ | 5933 | 0.1144 | -1.4977 |
|  | $r^{\prime \prime \prime}{ }^{\prime \prime} 24$ | $13615 \frac{1}{2}$ | 2858 | 7026 | $6151 \frac{1}{2}$ | 0.3827 | -0.3999 |
| Twinning plane | $\overline{\mathbf{I}} 22$ | $-3308$ | 3851 | 6957 | 5457 | -0.4403 | 0.6745 |

Table 3 gives the final computed values of the angles used for getting the approximate elements, and also of a few other important angles. For comparison, the averages of the measured values of the same angles are listed. There are some rather large differences as well as close agreements but the result is, on the whole, more satisfactory than was expected from the character of the crystals. The elements adopted may not be correct to more than three decimal places, but in order that the
angles in a table shall be mutually consistent, the computations were carried to five decimal places and all angles were computed to seconds.

Table 3.-Comparison of Angles

| Angle | Number of <br> Measurements | Used in <br> Average | Average of <br> Measurements | Computed <br> Values |
| :--- | :---: | :---: | :---: | :---: |
|  | 78 | 33 | $33^{\circ} 08^{\prime}$ |  |
| $c a u$ | 34 | 23 | 3400 |  |

Form letters in parentheses indicate forms in twin position.

## Habit and Detailed Morphology

Both earlier authors describe and draw the crystals as commonly tabular, parallel to a large face. The new measurements show, however, that this "face" is not the same form on all crystals-on some it is $\{101\}$ poorly developed, on others it is $\{\overline{1} 10\}$ in twinned position, which lies about $4^{\circ}$ from the orthodome zone. On still others it is not a single face but is rounded and striated, with irregular facets of $\{101\},\{\overline{1} 10\}$ twinned and perhaps of $\{\overline{1} 00\}$ twinned, the whole so rough and dull that only rarely can any good signals be seen.

On untwinned crystals (not yet observed) the dominant form would probably be $\{101\}$, and this in combination with the prism $\{110\}$ would give the crystals a habit roughly resembling a rhombohedron with one pair of opposite faces dominant. Figure 1 shows the writer's mental
picture of an untwinned tsumebite crystal of such a habit, with the back indicated in order better to bring out this resemblance.

The pinacoid $a$, seen on most crystals, is a narrow or linear, bright and easily recognized face. Of the prisms only $m$ is common or important. Every crystal group bears several large faces of it, but instead of being plane they are usually aggregates of bright facets, slightly divergent and giving confusing multiple signals. The orthodome $d$ is fairly common, but seldom yields a measurable signal, so that measurements have to be made on the brightest reflection. No attempt has been made in the figures to show it as anything but a cleanly developed plane face.


Fig. 4. Plan and clinographic projection of a twinned crystal of tsumebite that furnished the key to the mode of twinning. (Seen from above and from the rear.)
Fig. 5. Clinographic projection of a twinned crystal of tsumebite showing the zones of oscillatory combination, both untwinned and twinned. (Bottom and rear of crystal, inverted by rotation about the $b$-axis.)

The other domes and the pyramid are as a rule small, plane, brilliant three-, four-, or five-sided facets. The clinodome $u$, second commonest form, and the orthodome $f$ are found both alone and also together in oscillatory combination in narrow bands that may, if not closely examined, be mistaken for deeply striated faces (Fig. 5). These bands are characteristic of tsumebite crystals and are seen on all well-developed groups. On many they are double, one band being in twin position, and the zigzag suture between them is the trace of the composition face of the twinned crystal. The resultant V-shaped depression across the crystal establishes the orientation as, because of the mode of twinning, it is developed only on the lower side of the twinned crystals.

There are three habits of twinned crystals, differing only in perfection of development of the twinned member-the compact or "V" type, shown in Figs. 4 and 5; the "Y" type (commonest), shown in Fig. 2; and the " $X$ " type, not figured here. Twinning on a pyramid seems to be rare in monoclinic crystals, but Zepharovich has described augite crystals so twinned; on ( $\overline{1} 22$ ), like tsumebite, and in cruciform twins resembling the " X " type of tsumebite twins. (Jahrb. für Miner., etc., 1871, p. 60, Fig. 1.)

All the accompanying crystal figures are more or less idealized, especially those that are completely drawn. This is necessary, as the actual crystals are so intergrown in groups that only parts of them are to be seen, mingled with parts of others. To make "portrait" drawings would be well nigh impossible and they would be so intricate as to be unsatisfactory for portraying the crystals. Every face shown in Fig. 4 could be identified on the crystal but none had the perfection of outline shown in the figure.

## Composition

A number of the crystals, carefully separated from smithsonite and malachite by Dr. Berman, were analyzed by Mr. F. A. Gonyer, chemist of the Department of Mineralogy and Petrography at Harvard University. The result, with those of previous analyses, is given below.

Analyses of Tsumebite

|  | 1 | 2 | 3 | 4 | 5 | 6 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| PbO | 63.77 | 65.09 | 64.71 | 0.2874 | $=4 \times 0.0719$ | 65.84 |
| CuO | 11.79 | 11.97 | 12.13 | 0.1524 | $=2 \times 0.0762$ | 11.73 |
| $\mathrm{P}_{2} \mathrm{O}_{5}$ | 12.01 | 10.26 | 10.62 | 0.0747 | $=1 \times 0.0747$ | 10.47 |
| $\mathrm{H}_{2} \mathrm{O}+$ | 12.33 | n.d. | 12.09 | 0.6711 | $=9 \times 0.0746$ | 11.96 |
| ZnO | - | - | 0.54 |  |  |  |
| $\mathrm{CO}_{2}$ | - | - | 0.24 |  |  |  |
| Total | 99.90 | - | 99.79 | 1.1856 | $=16 \times 0.0740$ | 100.00 |

1-Analysis by F. Rüssberg and H. Dubigk, 1912.
2-Analysis by J. Frejka, 1912.
3-Analysis by F. A. Gonyer, 1937.
4-Molecular equivalents of 3 .
5. Molecular ratio of 3 .

6-Composition computed from formula below.
The atomic composition derived from column 5 of the table above is: $\mathrm{Pb}_{4} \mathrm{Cu}_{2} \mathrm{P}_{2} \mathrm{H}_{18} \mathrm{O}_{20}$, which can be written in the form: $\mathrm{Pb}_{2} \mathrm{Cu}\left(\mathrm{PO}_{4}\right)(\mathrm{OH})_{3}$ $.3 \mathrm{H}_{2} \mathrm{O}$. Tsumebite is, therefore, a hydrous basic phosphate of lead and
copper. The small amount of Zn and $\mathrm{CO}_{2}$ found by Gonyer can safely be ascribed to a tiny fragment of smithsonite adhering to one of the tsumebite crystals. Although the three analyses agree rather well they differ just enough so that a different formula may be written for each, but the average of the three, each recomputed to 100 per cent, agrees so closely with Gonyer's analysis as to give the same formula.

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