TARBUTTITE

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INTRODUCTION

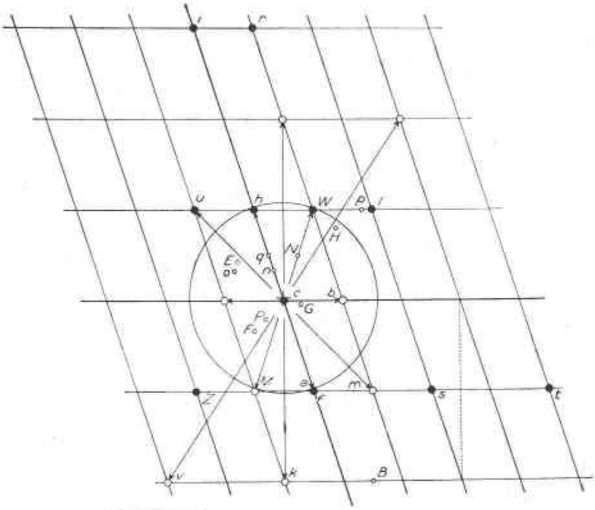
Tarbuttite, a basic zinc phosphate, was first described by Spencer (1907, 1908). His crystals were for the most part composed of subparallel groups with individual forms usually striated and rounded, with few well-defined faces in the primary zones so that, to use his own words, "the calculations are all the more awkward . . . and the elements given below can only be considered as a first approximation." Rosický (1913) adopted Spencer's setting and measured a large number of crystals on which he found 17 new forms but did not recalculate the elements.

The stereographic projection accompanying Spencer's paper shows a large obliquity of the base, a scarcity of forms in the vertical zone and several form-rich pyramidal zones. These facts suggested a search for a possible better choice of elements. To this end a complete morphological investigation together with an *x*-ray determination of the lattice constants was undertaken, the results of which appear in this paper.

MORPHOLOGY

A number of matrix specimens of tarbuttite from the type locality, Broken Hill mines, N. W. Rhodesia, now in the Harvard Mineralogical Museum, were carefully examined for suitable crystals. One superb specimen (Harvard number 92882) was found consisting of a matrix of black stalactitic limonite thickly sprinkled with a large number of colorless, transparent crystals varying in size from 0.1 to 1.0 millimeter. The faces were bright, sharp and free from striations. Their habit, short prismatic approaching pseudoisometric, presented considerable difficulty in the choice of the prismatic zone.

The crystals are usually attached to the matrix on a plane nearly parallel to the perfect cleavage. The choice of a prismatic zone was made difficult in these crystals through the absence of a pronounced direction of elongation and by the presence of large faces of what proved to be forms of highly complex indices (forms *G* and *E* of figure 2). But by setting the perfect cleavage ({001} of Spencer's position) vertical and by selecting the strongest zone of which it formed a part as the prism zone, a satisfactory orientation was secured. Measurements being made on the two-circle goniometer with this zone vertical, a gnomonic projection was obtained which is shown in figure 1. In this projection the choice of *b*[010] normal to the cleavage is obvious. For *a*[100] the selec-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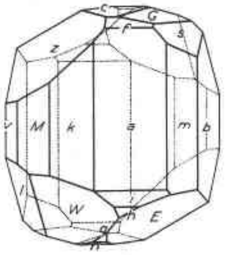
1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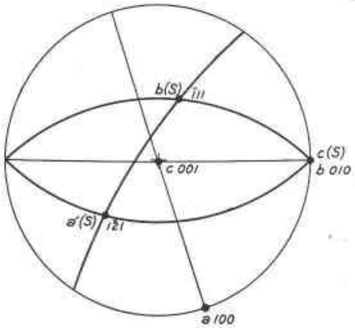
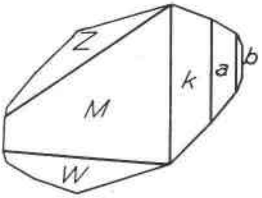
2


b(S) 1̄11
c 001
c(S)
b 010
a'(S) 1̄21
a 100

3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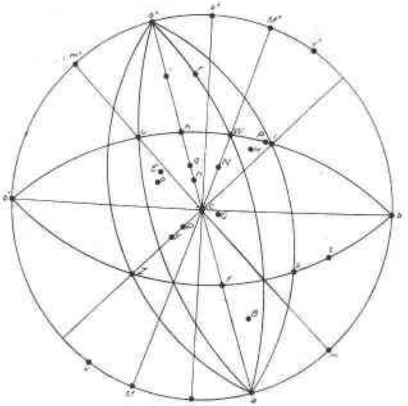
2a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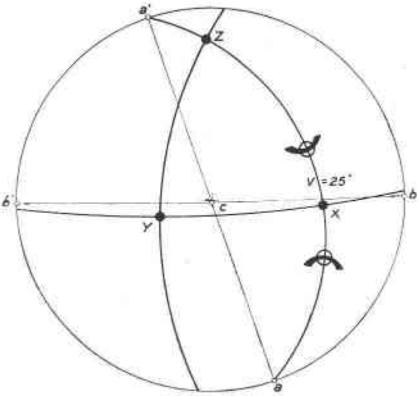
a'
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V = 25°
b'
c
b
Y
X
a

5

tion of either [*cf*] or [*cM*] is indicated; they proved by calculation to give essentially equal periods. The choice leaned toward the more pronounced zone contained in [*cf*]; this choice was found to lead to simpler indices and was therefore taken as [100].

Figure 1 is the gnomonic projection of the accepted forms of tarbuttite on a plane normal to the chosen vertical axis. The gnomonic plane is also considered as the first layer $|hk1|$ of the reciprocal lattice. The vertical planes ($hk0$) are represented by radial lines drawn from $c\{001\}$ to ($hk1$), the point ($hk1$) being inserted as a large blank circle, *m b k M v*, when it does not represent a known terminal form. These radial lines are thus normal to their respective vertical planes, and their lengths are inversely proportional to the spacings and reticular densities of the corresponding planes in the direct lattice.[1]

The points marked by large filled circles, *c f Z s t W l r h u i*, are nodes of the reciprocal lattice in the first layer and their spacings define the lattice translations. These face poles may be considered as actually in the plane of the gnomonic projection. The small blank circles, *G P F B N H p n q o E*, represent terminal planes which lie on higher lattice layers (hkn) and occupy fractional positions on the gnomonic projection. The representative lattice cell, therefore, may be defined as that cell whose respective reciprocal lattice points, either present or implied, are the three non-colinear points nearest the origin. The point nearest the center *c* represents the axial plane (001); the first layer point nearest *c*, namely *b*, is taken as (011); the next nearest not in zone [*cb*], namely *f*, as (101).

Figure 2 is a typical crystal of tarbuttite in normal position. Figure 2*a* is a crystal of tarbuttite after Spencer, redrawn in normal position.

The most prominent forms in the vertical zone are $a\{100\}$ and $b\{010\}$. The terminal planes are unusually well developed and give remarkably perfect signals. The largest and most frequently observed forms are $c\{001\}$, $G\{1.6.23\}$, $s\{121\}$, $Z\{1\bar{2}1\}$, $W\{\bar{1}11\}$, $l\{\bar{1}21\}$, $E\{\bar{3}\bar{4}7\}$, $u\{\bar{1}\bar{1}1\}$.

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[1] The obliquity of the base is so small that the large blank circles, which would normally appear on the reciprocal lattice projection of the zero layer-line slightly offset from the net intersections, are placed on these intersections to avoid confusion.

FIG. 1. Tarbuttite: gnomonic projection of the accepted forms.

FIG. 2. Tarbuttite: typical doubly terminated crystal from Broken Hill, Northern Rhodesia.

FIG. 2a. Tarbuttite: crystal drawing in new position after Spencer.

FIG. 3. Tarbuttite: relation of Spencer's setting to that of the new position.

FIG. 4. Tarbuttite: stereographic projection of the accepted forms.

FIG. 5. Tarbuttite: stereographic projection of the optical orientation and the position of the optic axes.

These appeared on nearly every crystal measured. The new form $q\{\bar{1}02\}$ was observed on three crystals as a small face in good position.

The singular development of the forms $G\{1.6.23\}$ and $E\{\bar{3}\bar{4}7\}$ is a unique feature of these crystals. On the eleven crystals employed for calculation, *G* was observed eight times and *E* ten times. Their positions in the projection are good and their measured values agree well with those calculated. Added evidence of their rationality is obtained by zonal calculation. The face pole *G* lies at the intersection of two zones $[1\bar{4}1]$ defined by the face poles $\{\bar{1}01\}$ and $\{212\}$, and $[\bar{6}10]$ defined by $\{001\}$ and $\{163\}$; the indices of this zone intersection are $\{1.6.23\}$ which is the symbol determined for *G*. Similarly, *E* lies at the intersection of the zone $[4\bar{3}0]$ passing through the face poles $\{001\}$, $\{\bar{3}\bar{4}3\}$, and the zone $[111]$ containing $\{101\}$, $\{1\bar{2}1\}$; the symbol of the intersection is $\{\bar{3}\bar{4}7\}$, which is the symbol of *E*. The comparatively simple indices of the zones passing through *G* and *E* may be taken as confirming their rational character.

Rosický observed these two forms and gave them the indices $G\{\bar{5}59\}$, $E\{\bar{3}84\}$, which in the new position correspond to $\{0.13.10\}$, $\{\bar{5},\bar{6},11\}$. These are but approximately similar to indices derived from the writer's observations. Comparison of calculated angles for the two sets of symbols (table 1) shows similarity for *E* and an unexplained gross discrepancy for the azimuth angle of *G*.

TABLE 1. TARBUTTITE: COMPARISON OF THE SETS OF INDICES OF *G* AND *E*

	ϕ	ρ
G $\{0.13.10\}$	7°39′	11°00′
$\{1.6.23\}$	20 35	10 47
E $\{\bar{5}.6.11\}$	−139 21½	31 58
$\{\bar{3}\bar{4}7\}$	−141 56½	31 42½

Rosický's crystals were of poor quality, which undoubtedly prevented him from determining the true indices of these two forms. Due to the remarkable perfection of development of these forms on the crystals studied here and the excellence of their position on the gnomonic projection, it was decided to adopt new indices while retaining the old letters.

Table 2 gives the measured maximum range, the best measured mean, the calculated ϕ and ρ of the forms, together with the number of times each form was observed. The perfection of the crystals studied is well brought out by the close agreement of the mean measured and the calculated values of ϕ and ρ.

TABLE 2. TARBUTTITE: COMPARISON OF THE MEASURED AND CALCULATED ϕ AND ρ.

Form		Faces	Measured Range		Best Measured Mean		Calculated	
			ϕ	ρ	ϕ	ρ	ϕ	ρ
c	001	11	90°40′– 82°30′	1°47′– 1°30′	87°17′	1°38′	87°00′	1°28½′
b	010	22	359 45 – 0 02	90°00′	0 00½	90 00	0 00	90 00
a	100	20	72 28 – 72 15	90 00	72 19	90 00	72 19	90 00
m	110	4	46 00 – 43 39	90 00	45 15	90 00	45 35½	90 00
k	$2\bar{1}0$	17	91 10 – 90 33	90 00	90 45	90 00	90 39½	90 00
M	$1\bar{1}0$	19	109 15 – 108 47	90 00	109 04	90 00	108 52	90 00
v	$2\bar{3}0$	1	123 56	90 00	123 56	90 00	123 54½	90 00
f	101	11	72 41 – 72 06	42 56 –45 20	72 25	45 34	72 41	45 35
n	$\bar{1}03$	10	−108 17 – 107 52	17 18 –16 50	−108 00	16 57	−108 54	17 04
**q*	$\bar{1}02$	3	−108 19 −−107 37	25 12 –24 57	−108 11	25 03	−108 28½	25 18½
h	$\bar{1}01$	11	−107 51 −−107 38	44 11 –43 53	−107 49	44 07	−108 04	44 09
i	$\bar{3}01$	9	−108 18 −−107 08	71 38 –71 18	−107 44	71 21	−107 37	71 19½
G	1.6.23	8	20 58 – 20 15	11 08 –10 57	20 30	11 00	20 35	10 47½
s	121	5	32 01 – 31 14	61 55 –61 26	31 59	61 34	32 02	61 26
P	$1\bar{2}5$	7	130 39 – 129 50	15 57 –15 06	130 35	15 50	131 14½	15 59½
F	$1\bar{2}3$	10	132 51 – 132 03	25 04 –24 34	132 40	24 52	132 42½	24 57½
Z	$1\bar{2}1$	11	134 29 – 134 07	53 44– 53 23	134 13	53 40	134 15½	53 41
N	$\bar{1}12$	7	− 69 18 −− 68 40	25 47 –25 13	− 69 15	25 34	− 69 58½	25 31½
W	$\bar{1}11$	10	− 70 46 −− 69 47	44 41 –44 25	− 70 35	44 26	− 70 41	44 21½
l	$\bar{1}21$	6	− 44 36 −− 43 37	53 25 –53 00	− 44 11	53 02	− 44 06	52 59
r	$\bar{3}11$	1	−95 36	70 30	− 95 36	70 30	− 95 39½	70 34
E	$\bar{3}\bar{4}7$	10	−141 45 −−141 35	31 40 –31 30	−141 33	31 37	−141 56½	31 42½

* New form.

CORRELATION OF SETTING

The relation of Spencer's setting to the writer's is shown in figure 3. From the figure, the form-to-form transformation formula can be directly derived when it is recognized that Spencer's *c* is one-half Richmond's *b*, so that [010] must be multiplied by 2.

Spencer	*Richmond*
a' $\bar{1}00(100)$	$1\bar{2}1(\bar{1}2\bar{1})$
b 010	$\bar{1}11$
c 001	020

The transformation formula is, therefore, $\overline{11}0/212/\bar{1}10$.

Table 3 shows the forms of tarbuttite observed by Spencer, Rosický and Richmond. The forms represented by a letter in the column *Richmond* are the forms observed by him and accepted as established. Certain additional forms observed by Spencer or Rosický but not by

TABLE 3. TARBUTTITE: CORRELATION OF FORM LETTERS

Form	*Richmond*	*Spencer-Rosický*		
001	*c*	*g*	$\bar{2}21$	*g*
010	*b*	*c*	001	*c*
100	*a*	*d*	$\bar{2}\bar{2}3$	*d*
110	*m*	—	$\bar{2}\bar{2}5$	*y*
430	?	—	$\overline{44}9$	*L*
210	?	—	$\overline{11}2$	*x*
$2\bar{1}0$	*k*	*k*	$\bar{1}11$	*k*
$1\bar{1}0$	*M*	*e*	$\bar{2}\bar{2}1$	*e*
$10.\overline{11}.0$	?	—	$\bar{5}\bar{5}2$	*z*
$2\bar{3}0$	*v*	*m*	110	—
$0\bar{7}4$	?	—	$\bar{4}45$	*C*
$0\bar{3}1$	?	—	—	—
$0.\overline{11}.2$	?	—	$1\bar{1}5$	*D*
101	*f*	*f*	$\bar{1}01$	*f*
$\bar{1}03$	*n*	—	$\bar{2}01$	*n*
$\bar{1}02$	*q**	—	—	—
$\bar{1}01$	*h*	*h*	$0\bar{2}1$	*h*
$\bar{3}01$	*i*	*i*	$\bar{1}\bar{2}2$	*i*
1.6.23	*G*	—	—	—
0.13.10	?	—	$\bar{5}59$	*G*
121	*s*	*s*	$\bar{1}02$	*s*
141	*t*†	*t*	$\bar{1}03$	*t*
412	*B*†	—	$\bar{3}14$	*B*
$1\bar{2}5$	*P*	—	$\bar{3}21$	*P*
$1\bar{2}3$	*F*	—	$\bar{4}21$	*F*
$5\bar{4}3$	?	—	$\bar{8}25$	*M*
$1\bar{2}1$	*Z*	*a*	100	*a*
$\bar{9}.10.15$	?	—	$\bar{3}.12.2$	*w*
$\bar{1}12$	*N*	—	$\bar{2}61$	*N*
$\bar{8}.13.10$	*H*†	—	$\bar{1}93$	*H*
$\bar{1}11$	*W*	*b*	010	*b*
$\bar{5}95$	*p*†	—	052	*p*
$\bar{1}21$	*l*	*l*	021	*l*
$\bar{3}11$	*r*	*r*	$\bar{2}\bar{4}3$	*r*
$\bar{3}21$	?	—	—	—
$\bar{1}\bar{2}3$	*o*†	*O*	$1\bar{2}1$	—
$\bar{5}.\bar{6}.11$	?	—	384	*E*
$\bar{3}\bar{4}7$	*E*	—	—	—
$\bar{1}\bar{1}1$	*u*†	*u*	$0\bar{1}1$	—

* New form.

TABLE 4. TARBUTTITE: $Zn_2PO_4(OH)$

Triclinic; pinacoidal-$\bar{1}$

$a:b:c=0.6296:1:0.5971;\ \alpha=89°37\tfrac{1}{2}',\ \beta=91°28\tfrac{1}{2}',\ \gamma=107°41'$

$p_0:q_0:r_0=0.9954:0.6265:1;\ \lambda=89°55\tfrac{1}{2}',\ \mu=88°34\tfrac{1}{2}',\ \nu=72°19'$

$p_0'=0.9957,\ q_0'=0.6267;\ x_0'=0.0258,\ y_0'=0.0014$

	Form	φ	ρ	A	B	C
c	001	87°00′	1°28½′	88°34½′	89°55½′	—
b	010	0 00	90 00	72 19	—	89°55½′
a	100	72 19	90 00	—	72 19	88 34½
m	110	45 35½	90 00	26 43½	45 35½	88 53½
k	$2\bar{1}0$	90 39½	90 00	18 20½	90 39½	88 31½
M	$1\bar{1}0$	108 52	90 00	36 33	108 52	88 37½
v	$2\bar{3}0$	123 54½	90 00	51 35½	123 54½	88 49
f	101	72 41	45 35	44 25	77 43½	44 16
n	$\bar{1}03$	−108 54	17 04	107 04	95 27½	18 29½
*q	$\bar{1}02$	−108 28½	25 18½	115 18½	97 47	26 44
h	$\bar{1}01$	−108 04	44 09	134 09	102 28½	45 34½
i	$\bar{3}01$	−107 37	71 19½	161 19½	106 40	72 45½
G	1.6.23	20 35	10 47½	83 20½	79 54½	10 17
s	121	32 02	61 27	47 56	41 53	60 35½
t	141	19 07½	71 25	55 24	26 25	70 52
B	412	64 26½	64 52	26 15½	67 00½	63 30½
P	$1\bar{2}5$	131 14½	15 59½	81 49½	100 49½	14 57½
F	$1\bar{2}3$	132 42½	24 57½	77 58	106 37½	23 56½
Z	$1\bar{2}1$	134 15½	53 41	67 44	124 13	52 41½
N	$\bar{1}12$	− 69 58½	25 31½	109 56	81 31	26 53
H	8.13.10	− 51 56½	42 57½	112 33½	65 09½	44 05
W	$\bar{1}11$	− 70 41	44 21½	124 27	76 37½	45 44
p	$\bar{5}95$	− 48 08½	51 06	126 18½	58 43	51 56
l	$\bar{1}21$	− 44 06	52 59	110 48½	55 01½	53 57½
r	$\bar{3}11$	− 95 39½	70 34	157 16	95 20	72 02½
o	$\bar{1}\bar{2}3$	−150 41	30 40½	111 54½	116 25	30 42½
E	$\bar{3}\bar{4}7$	−141 56½	31 42½	115 44½	114 26½	32 42
u	$\bar{1}\bar{1}1$	−135 09	52 37	134 49	124 17	53 43½

* New form.

Richmond are indicated by a dagger after the letter. Forms not observed by Spencer or Rosický are followed by a dash. Forms represented by a ? in column *Richmond* were discredited by him for one or more of the following reasons: (1) observed but once and in poor position, (2) calculated values not in agreement with actual measurements, (3) complexity of symbols and poor position.

Using the method outlined by Wolfe (1937), we transform Spencer's elements to those in the writer's setting and obtain: $a:b:c=0.6332:1:0.6047$; $\alpha=89°14\frac{1}{2}'$, $\beta=92°26\frac{1}{2}'$, $\gamma=108°00'$.

The elements from the new measurements are: $a:b:c=0.6296:1:0.5971$; $\alpha=89°37\frac{1}{2}'$, $\beta=91°28\frac{1}{2}'$, $\gamma=107°41'$.

The two sets of elements are not in close agreement. Spencer states that his elements are only "a first approximation," being derived from crystals unsuitable for accurate measurements. The crystals here studied are of such exceptional quality that measured and calculated values agree closely. The new elements are therefore adopted and employed to derive the formal angle table for the accepted forms of tarbuttite in the new setting (table 4).

Figure 4 is a stereographic projection of the accepted forms of tarbuttite.

OPTICS

The optical properties of tarbuttite were determined on a small crystal mounted on the universal stage, and by the immersion of crystal fragments. The optical data are summarized in table 5.

TABLE 5. TARBUTTITE: OPTICAL DATA

	ϕ	ρ	n(Na)		
X	7°	58°	1.660	±0.003	negative
Y	159	25	1.705		2V=50°
Z	−86	80	1.713		no pleochroism

The optical orientation and the positions of the optic axes in relation to the principal planes of the crystal are represented stereographically in figure 5.

PSEUDOSYMMETRY

The new setting of tarbuttite brings out certain pseudosymmetrical elements which are graphically illustrated in figures 1 and 6. In figure 1 the dotted lines outline one pseudoisometric cell. The direction of the unit prism *m* is approximately in the 45° position and *k* at 90°; *c* is close to the center of the projection. Figure 6 is a clinographic drawing of the direct lattice cell of tarbuttite (small) and shows the relation of the unit cell to that of the pseudoisometric (heavy dashes).

STRUCTURAL LATTICE

X-ray measurements were made on a single carefully selected crystal 0.5 millimeter in the longest direction. The six lattice elements were determined by rotation and Weissenberg photographs of the zero and first layer-lines rotating the crystal successively about the three chosen crystallographic axes.

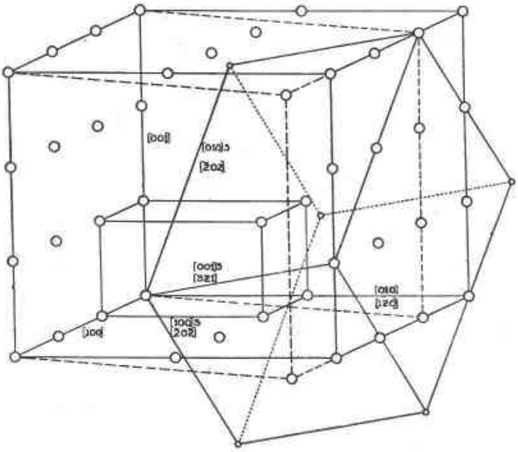

FIG. 6. Tarbuttite: relation of the several direct lattice cells.

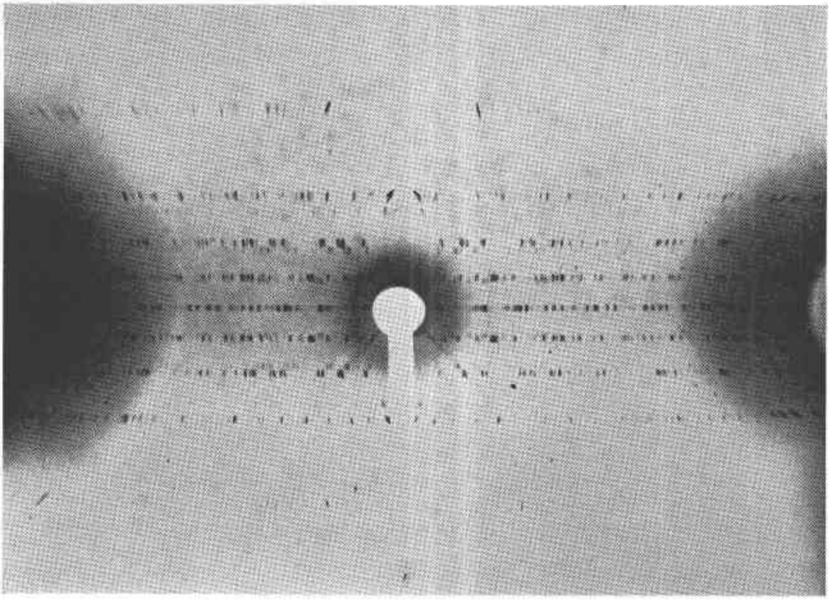

FIG. 7. Tarbuttite: rotation photograph about the *c*-axis; unfiltered copper radiation.

Excellent photographs were obtained with copper radiation. The films were practically unfogged by scattered radiation due to the shortness

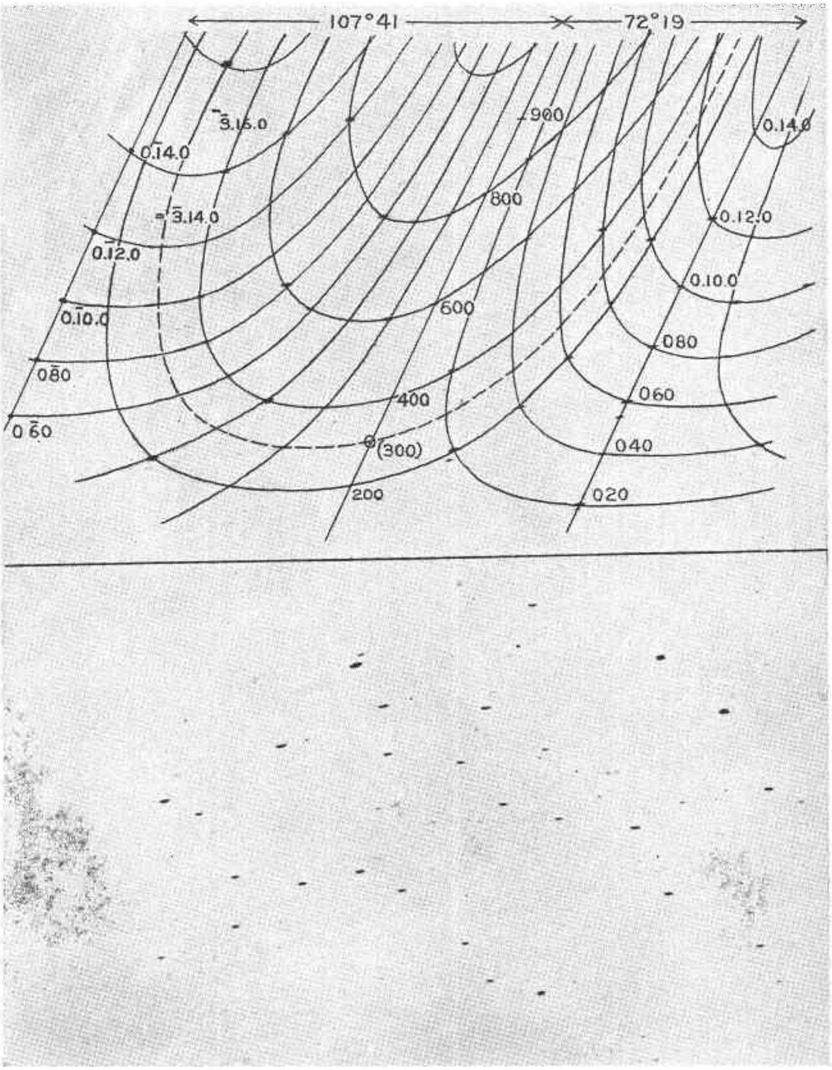

FIG. 8. Tarbuttite: zero layer-line photograph about *c*-axis; unfiltered copper radiation.

of the exposure time. The diffraction spots were exceptionally sharp so that it was possible to measure and calculate the lattice elements with considerable accuracy.

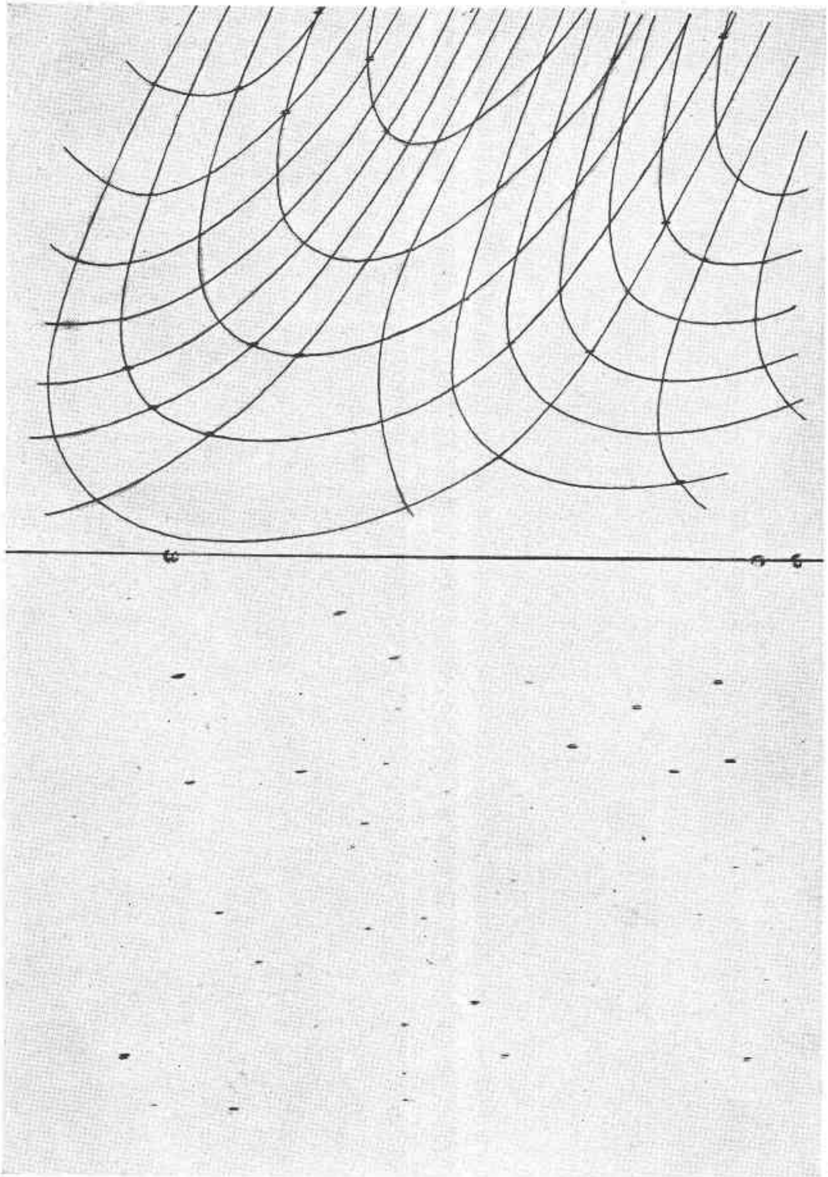

FIG. 9. Tarbuttite: first layer-line photograph about *c*-axis; copper radiation; nickel filter.

The exceptional quality of the photographs is shown in figures 7, 8, and 9. The rotation and zero layer-lines were taken without a filter (figures 7, 8), while a nickel filter was used for the first layer-line (figure 9). The zone lines have been drawn in on the zero and first layer line photographs and the intersection of the zone lines with the axial directions indexed. These photographs were all taken about the *c*-axis.

The zero layer-line photographs taken about the three zone axes gave three pairs of values for the spacings of the axial planes. The reciprocal axial angles were determined by lattice spacing measurements along lattice cell diagonals and by triangulation calculations. The lattice constants measured and computed are shown in table 6.

TABLE 6. TARBUTTITE: STRUCTURAL LATTICE CONSTANTS

From rotation photographs	From Weissenberg photographs			
Å			Å	
$a_0= 8.062$	$d_{100}= 7.706$	$\alpha^*=89°51'$	$a_0= 8.097$	$\alpha= 89°34\frac{1}{2}'$
$b_0=12.86$	$d_{010}=12.29$	$\beta^*=88\ 27$	$b_0=12.91$	$\beta= 91\ 35\frac{1}{2}$
$c_0= 7.687$	$d_{001}= 7.685$	$\gamma^*=72\ 14$	$c_0= 7.688$	$\gamma=107\ 47$

A study of the lattice parameters shows that the three chosen axes of rotation, which were previously taken as the three crystallographic axes, are also the three shortest noncoplanar lattice periods.

The direct lattice elements calculated from the Weissenberg photographs give the following ratio, which agrees well with that computed from the geometrical elements.

$$a_0:b_0:c_0 = 0.6271:1:0.5957; \quad \alpha = 89°34\tfrac{1}{2}', \quad \beta = 91°37\tfrac{1}{2}', \quad \gamma = 107°47'$$
$$a:b:c = 0.6296:1:0.5971; \quad \alpha = 89°37\tfrac{1}{2}', \quad \beta = 91°28\tfrac{1}{2}', \quad \gamma = 107°41'$$

The relation of Spencer's lattice cell (large cell with solid and dotted lines) to that in the new position is shown in figure 6.

The method outlined by Wolfe and used to transform Spencer's elements to those in the new position may also be employed to calculate the edge lengths of the Spencer cell in the new position as well as the volume of that cell. This method makes use of the transformation formula Spencer to Richmond ($\overline{1}\overline{1}0/212/\overline{1}10$) and the absolute lengths of the chosen unit cell. Matrix calculation of the Spencer to Richmond transformation together with translation formulae give the following relationship:

$$
\begin{array}{llll}
a' & [100]=[\bar{2}0\bar{2}]=22.03\text{Å} & \qquad & a_0=\ 8.097\text{Å} \\
b' & [010]=[\bar{2}02]=22.58 & & b_0=12.91 \\
c' & [001]=[321]=30.46 & & c_0=\ 7.69
\end{array}
$$

$$
\begin{array}{ll}
\alpha' & [010]\wedge[001]=[\bar{2}02]\wedge[321]=100°06\tfrac{1}{2}' \\
\beta' & [001]\wedge[100]=[321]\wedge[\bar{2}0\bar{2}]=123\ 54\tfrac{1}{2} \\
\gamma' & [100]\wedge[010]=[\bar{2}0\bar{2}]\wedge[\bar{2}02]=\ 89\ 42
\end{array}
$$

From the volumetric formula the volume of the Spencer cell is 12,297.45 cu. Å. The volume of the new unit cell is 765; therefore the volume of Spencer's cell is 16.06 cu. Å (ca. 16.00) times that of the unit cell, which is also a reflection of the accuracy of the preceding calculations.

CONTENTS OF THE UNIT CELL

The chemical analysis of tarbuttite by Spencer gives the formula $Zn_2PO_4(OH)$. The determined elements of the structural lattice give the volume of the unit cell, $V_0=764.9$, which, with the given density 4.15, makes the cell molecular weight, $M_0=1924$. The analysis then gives the number of molecules in the unit cell as shown in table 7.

TABLE 7. TARBUTTITE: MOLECULAR CONTENT OF THE UNIT CELL

	1	2	3	4
ZnO	66.6	0.822	15.81	16
P_2O_5	29.2	0.205	3.94	4
H_2O	3.8	0.212	4.08	4

1. Tarbuttite, Broken Hill mines, N.W. Rhodesia; Spencer, *analyst.*
2. Molecular proportions from analysis reduced to 100%.
3. Number of molecules in the unit cell.
4. Number of molecules in the unit cell reduced to the nearest whole number.

The molecular content of the unit cell is, therefore, 16ZnO, $4P_2O_5$, $4H_2O$, giving the cell formula $8[Zn_2PO_4(OH)]$.

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