Geometrical and Optical Properties, and Crystal Structure of Tenorite.

By

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(With 4 figures.)

Part I. Geometrical and Optical Properties.

The goniometrical measurements of N. Story-Maskelyne¹) on crystals of tenorite (also called melaconite) found with cuprite and chrysocolla in a chloritic veinstone from Lostwithiel, Cornwall, satisfy the symmetry requirements of the monoclinic system, and the crystal habit illustrated in the drawing of Story-Maskelyne is clearly that of the holohedral class of the monoclinic system. Moreover, as A. Scacchi²) has pointed out, the goniometrical measurements of J. Jenzsch³) on artificial crystals of cupric oxide formed near a flue in a smelter-hearth during roasting of copper matte with sodium chloride at Freiberg, yield calculated elements agreeing with those of Story-Maskelyne, and the crystals drawn by Jenzsch exhibited the same habit and twin-law as those of Story-Maskelyne. Jenzsch interpreted his crystals as orthorhombic but his measurements do not satisfy orthorhombic symmetry requirements either qualitatively or quantitatively.

Numerous inconsistencies and errors in detail occur in the papers of Story-Maskelyne, of Jenzsch, and of Scacchi. For this reason we have carried out geometrical and optical, as well as X-ray measurements, sufficient to establish our conclusions without the use of previous experimental results. At the same time our conclusions are in agreement with previously reported experimental facts. Our conclusions rest on optical, geometrical, and X-ray study of the thin natural tenorite crystals deposited on the lavas of Mount Vesuvius, on X-ray study of chemically pure artificial cupric oxide powder, and finally on geometrical and X-ray study of single faceted crystals of tenorite prepared for the purpose by recrystallization in molten sodium hydroxide.

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1) Verh. Petersb. Min. Ges. **1** (1866) 147.

2) Contribuzioni mineralogiche per servire alla storia dell'incendio vesuviano del mese di Aprile 1872, p. 12. Atti Accad. Sc. fis. e mat. Napoli, vol. **6**, 1875.

3) Poggendorffs Ann. Phys. u. Chem. **107** (1859) 647.

By comparison of their X-ray powder diffraction photographs we have first established the identity of the chemically pure artificial cupric oxide powder[1]) with tenorite crystals from Vesuvius[2]) carefully freed by hand under the binocular microscope from admixed grains of lava and other impurities. We have next proved by means of their interfacial angles and X-ray diffraction pattern that the single faceted artificial crystals formed in molten sodium hydroxide cannot be a different modification from the Vesuvian crystals and the chemically pure artificial powder.

Measurements made by us with a two-circle reflection goniometer on a single faceted crystal of tenorite formed in molten sodium hydroxide are embodied in table I. This crystal was also analyzed by means of

Table I. **Measurements with Two-circle Reflection Goniometer on an Artificial Single Crystal of Tenorite.**

Miller Symbol	V	H	φ	ϱ
$\bar{1}10$	194° 32′	72° 32′	— 36° 29′	90° 00′
$\bar{1}\bar{1}0$	87° 34′	72° 32′	— 143° 27′	90° 00′
$1\bar{1}0$	14° 30′	72° 39′	+ 143° 29′	89° 53′
110	267° 26′	72° 40′	+ 36° 25′	89° 52′

Table II. **Prism Angle of Tenorite, $110 \wedge \bar{1}10$.**

Tunell, Posnjak, Ksanda	
Measured on reflection goniometer	72° 59′
Measured with X-ray goniometer	72° 51′ ± 30′
Calculated from unit cell dimensions	73° 12′
Jenzsch	
Measured on reflection goniometer	72° 57$\frac{1}{3}$′
Story-Maskelyne	
Measured[3]) on reflection goniometer	73° 18′

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1) Two preparations were used. One was made by the J. T. Baker Chemical Company (Lot No. 121312) and the other by the Baker and Adamson Chemical Company.

2) Harvard University Specimen No. 83357 (Holden Collection).

3) Story-Maskelyne reported the measured angle cf [$100 \wedge 110$ in the orientation of the present writers] $= 53° 21'$. Then the angle $ff' = 180° - 2 \times 53° 21'$; this value is here given as Story-Maskelyne's measurement of ff' although it is not certain whether he measured the angles from c to the two faces f and f' and recorded as the average $cf = 53° 21'$ or whether he only measured the one angle from c to f. In the latter case the angle $ff' = 73° 18'$ is not strictly a measured angle but is still obtained more directly than Story-Maskelyne's calculated value of this angle, which is 73° 24′.

Table III. Geometrical Elements of Tenorite.

	a	*b*	*c*	*β*
Tunell, Posnjak, Ksanda (X-ray goniometer)	1.365	1	1.498	99° 29′
Jenzsch, Scacchi (reflection goniometer)	1.3714	1	1.4944	99° 39′
Story-Maskelyne (reflection goniometer)	1.3604	1	1.4902	99° 32′

the **Weissenberg** X-ray goniometer and a comparison of the angles obtained by the two methods, also a comparison with the angles measured by previous observers is given in table II. In the present investigation the *a*- and *c*-axes of **Story-Maskelyne** have been interchanged in order to render possible the application of the "Röntgenographische Auslöschungstabellen" of K. **Herrmann** in the subsequent structural determination[1]. Since the terminal faces of our artificial crystals were too small to give visible signals and no measurements of terminal faces could be made on the reflection goniometer, computation of all the geometric elements could not be carried out from the measurements obtained with the reflection goniometer. However, a complete and rigorous determination of the absolute unit cell dimensions was accomplished by means of the **Weissenberg** X-ray goniometer alone[2], and the geometric elements computed therefrom are given in table III together with those of **Story-Maskelyne** and those computed by **Scacchi** from **Jenzsch**'s measurements, the last two sets of elements being transformed to our own axes.

According to **Story-Maskelyne**[3] tenorite has an easy cleavage parallel to the faces designated by the present authors as (111) and a less easy cleavage parallel to the faces designated by us as (100)[4]. According to **Jenzsch**[5] tenorite cleaves very distinctly parallel to the faces designated by us as ($\bar{1}$11) and also parallel to the faces designated by us as ($\bar{1}$01). We have not been able to verify or disprove either of these statements and can only report that tenorite has two planes of cleavage the traces of which on (001) coincide with the zone axes [110] and [1$\bar{1}$0]; this obser-

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[1] For the purposes of descriptive mineralogy the orientation of **Story-Maskelyne** might well be retained.

[2] The determination of the unit cell dimensions by means of measurements on X-ray films is discussed in Part II.

[3] Op. cit., p. 150.

[4] **Scacchi** erroneously quoted **Story-Maskelyne** as having stated that tenorite has cleavages parallel to ($\bar{1}$11) and (011) (orientation of **Story-Maskelyne**). **Story-Maskelyne** actually reported, in his orientation, cleavages parallel to (111) and (001).

[5] Op. cit., p. 651.

vation would be consistent with cleavage parallel either to the positive unit pyramid or to the negative unit pyramid or even parallel to certain other faces. Our conclusion regarding cleavage is based on measurement of the angle between the cleavage traces on the plane of flattening of the thin tenorite crystals formed on the lava beds of Mount Vesuvius, and on the optical study of these crystals described in the following paragraphs.

We have examined a large number of the thin, minute crystals from Vesuvius under the microscope. Most of them are very narrow and somewhat curved or twisted in space. On the largest, thickest, and flattest of these microscopic crystals we measured the angle between the traces of the two perfect cleavage planes on the plane of flattening to be 72°15′ by rotation of the microscope stage, taking care that the crystal was lying parallel to the stage. Within the error of setting, the extinction directions coincide with the bisectors of the angles between the two cleavage traces, and the error of setting the crystal in the position of extinction did not exceed 1°1). We also studied the same crystal with convergent light using an oil immersion lens and a powerful strip-filament lamp. A biaxial interference figure was observed, with a bisectrix lying just inside the field (the crystal plate being horizontal) but it was not possible to decide with certainty whether the bisectrix was acute or obtuse; the optic sign of tenorite therefore remains at the present time unknown2).

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1) As an average of four settings **Tunell** found the extinction direction to make an angle of $^3/_4$° with the bisector of the angle between the cleavage traces; Dr. J. W. **Greig** kindly made the same experiment on the same crystal and as an average of four settings he found that the extinction direction exactly coincided with the bisector of the cleavage traces.

2) In a previous paper (E. **Posnjak** and G. **Tunell**, Amer. J. Sci., **18** (1929) 13) **Tunell** reported that the optic sign of tenorite is negative, stating that: "Additional important optical data were furnished by lath-shaped artificial crystals of cupric oxide, with irregular terminations due to corrosion, prepared by the authors in molten sodium hydroxide. These exhibited parallel extinction and a negative acute bisectrix sensibly perpendicular to the plane of flattening, γ the elongation being dark brown and β being light brown. They could thus be interpreted as monoclinic crystals with the observed extinction direction parallel to the trace of the symmetry plane and the bisectrix sensibly perpendicular to the plane of flattening by chance, or as orthorhombic crystals, but it is highly improbable that such features would be shown by triclinic crystals." Although the X-ray powder diffraction pattern of the sample from which the two crystals described in the quotation were taken was that of tenorite and the pleochroism of the two crystals in question was that of tenorite, it is now certain that these two crystals were not tenorite. Hence the conclusion on page 13 of the article cited that tenorite is optically negative with dispersion, $\varrho < v$, is not valid and must be discarded. The bulk of the sample from which the two crystals came was tenorite and the identity of the two crystals that

The trace of the axial plane was found to coincide with the bisector of the acute angle between the cleavage traces. The bisector of the acute angle was also the positive vibration direction of the crystal plate. The crystal plate was strongly pleochroic with the bisector of the acute angle dark brown and the bisector of the obtuse angle light brown.

By means of the graduated glass hemisphere described by F. E. Wright[1]) we have rotated one of the Vesuvius crystals about the bisector of the obtuse angle between the cleavage traces. During this rotation the crystal remained in extinction (within the error of setting the crystal in the position of extinction). The settings of the stage at which the crystal extinguished were as follows: When the crystal lay with its plane of flattening parallel to the stage the setting of the stage for extinction was 0°; the crystal was rotated 16° about the bisector of the obtuse angle and the stage setting for extinction was $^1/_2$°; the crystal was returned to the original position and the stage setting for extinction was $^1/_2$°; the crystal was rotated 24° about the bisector of the obtuse angle and the stage setting for extinction was $^1/_2$°; the crystal was again returned to its original position with its plane of flattening parallel to the stage and the setting of the stage for extinction was $-{}^1/_2$°. It therefore follows that one of the principal directions of the optical indicatrix lies in the plane of flattening of the crystal and coincides with the bisector of the obtuse angle between the cleavage traces; moreover, from the observations made with convergent light it follows that this principal direction of the indicatrix is the optic normal, β. The angle of the cleavage traces, 72°15′, is equal (within the error of measurement) to that between the zone axes, [110] and [1$\bar{1}$0], in the unit cell of tenorite established by X-ray analysis which is calculated to be 72°28′. Hence we conclude that the plane of flattening of the crystals is (001) in the orientation of the present authors[2]) and that the optic normal of tenorite coincides with the *b*-axis.

Another crystal was rotated on the Fedorov stage about the bisector of the acute angle between the cleavage traces as well as about the bisector of the obtuse angle. During the rotation about the bisector of the acute angle the stage setting for extinction was rapidly

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were not tenorite remains unknown. The remainder of the conclusions regarding the crystallography of tenorite previously published by Posnjak and Tunell were not based on the two crystals here discussed and have ample support in the earlier and present investigations.

1) The methods of petrographic-microscopic research, Carnegie Institution of Washington, Publication No. 158 (1911) 174.

2) This plane has the symbol (100) in the orientation of Story-Maskelyne.

displaced whereas rotation about the bisector of the obtuse angle produced no observable displacement.

Scacchi[1]) has given an elaborate description and many drawings of the Vesuvius tenorite crystals. His interpretation of the observed forms was based on two assumptions: the first assumption was that the Vesuvius tenorite crystals are flattened parallel to the monoclinic symmetry plane; the second assumption was that the Vesuvius tenorite constitutes a different polymorphic modification of cupric oxide from the melaconite crystal of Story-Maskelyne and the artificial crystal of Jenzsch but related to the last two through "polysymmetry". Some years later, however, Zambonini[2]) stated that there could no longer be any question of the identity of the Vesuvius tenorite with the melaconite of Story-Maskelyne, and that the crystals of tenorite are tabular on the plane designated by Story-Maskelyne as (100)[3]), as Story-Maskelyne had considered probable. The present investigation has proved that these statements of Zambonini are correct.

E. Kalkowsky[4]) made a rotation experiment by the following method. He cemented a thin Vesuvius tenorite twin-crystal between two pieces of cover-glass with balsam, attached the cover-glass combination to a needle by means of wax in such a manner that the long dimension of the twin-crystal was parallel to the needle, and passed the needle through a block of wood. The hole for the needle in the block of wood was made parallel to the microscope stage. The rotation of the needle was measured by means of a pointer attached to it and a circle attached to the block of wood. The twin-crystal was rotated and the extinction angle of each of the twins was read in different positions.

Kalkowsky[5]) concluded that: "die trikline Form seiner Blättchen läßt sich sehr leicht erklären nach den Angaben, welche Jenzsch über die Krystallform künstlichen Kupferoxydes, und Maskelyne über die des Melaconites von Lostwithiel in Cornwall gegeben haben. Danach sind die Tenorite flache Blättchen infolge vorherrschender Ausdehnung der Querfläche . . . Der Tenorit ist triklin, weil der eine optische Hauptschnitt mit starker Absorption polarisierten Lichtes den Winkel zwischen der linken und rechten Domenfläche nicht halbiert, weil die letzteren sich durch ungleich gute Spaltbarkeit als ungleichwertig zu erkennen geben,

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1) Op. cit.

2) Mineralogia Vesuviana **1910**, 68.

3) This plane has the symbol (001) in the orientation of the present authors.

4) Z. Kristallogr. u. Min. **3** (1879) 285.

5) Op. cit., p. 287.

und schließlich, weil zwei optische Elastizitätsachsen nicht in der Ebene der Blättchen liegen." Kalkowsky's statement of his own measurements is confused and inconsistent and only vaguely supports his first contention. As has already been indicated, the present authors found, on the contrary, that the extinction direction does bisect the angle between the two cleavage traces within the error of setting the crystal in the extinction position, which error was not more than 1°. The determination of the equality or inequality of the two cleavages is a matter of judgment. However, the reason given by Kalkowsky for believing that the cleavage oblique to the suture is better than that parallel to the suture is that the former was observed more often than the latter; he does not say that any effort was made to develop the cleavages artificially, and thus his own statement lacks weight since a crystal may have a perfect cleavage and not show it at all if it has never been struck or jarred. Actually we find that both cleavage traces of the thin Vesuvius crystals are directions of highly perfect separation, and that they can be developed artificially with equal ease by light pressure with a needle point. Kalkowsky's third reason for believing that tenorite is triclinic is irrelevant to the question; it is not necessary that two axes of elasticity lie in the "Querfläche" (front pinacoid)1) in order that the crystal be monoclinic.

We have proved that in respect to the optical and cleavage properties of tenorite any deviation from the exact requirements of monoclinic symmetry cannot exceed our limits of error in measurement and must be very small, and we prove in the second part of this paper that the same is true of the structural properties; moreover, we have proved that all the supposed evidence for its triclinic symmetry is illusory. Therefore we conclude that it is really monoclinic as Story-Maskelyne stated.

Part II. Crystal Structure.

Previous Work. The crystal structure of tenorite has been investigated by Niggli2), but his experimental data were obtained from powder photographs only. Niggli concluded that the copper atoms occupy the positions, $\frac{1}{4}, \frac{1}{4}, 0$; $\frac{3}{4}, \frac{3}{4}, 0$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$, and the oxygen atoms the positions, $\frac{1}{2}, \frac{1}{4}, \frac{3}{4}$; $0, \frac{3}{4}, \frac{3}{4}$; $\frac{1}{2}, \frac{3}{4}, \frac{1}{4}$; $0, \frac{1}{4}, \frac{1}{4}$, in a cell3)

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1) Kalkowsky apparently intended that his third reason should rule out the possibility of monoclinic symmetry even if the hypothesis of Scacchi were adopted that tenorite is monoclinic flattened parallel to the symmetry plane; we now know, however, that tenorite is flattened parallel to the base (orientation of present authors), not the symmetry plane.

2) Z. Kristallogr. 57 (1922) 269.

3) "Allseitig flächenzentriertes Elementarparallelepiped"; this is not a unit cell in Niggli's structure.

of dimensions, $a_0 = 4.67$ Å, $b_0 = 3.43$ Å, $c_0 = 5.12$ Å[1]), $\alpha = 90°$, $\beta = 99° 32'$, $\gamma = 90°$. He concluded further that the symmetry of tenorite is in reality triclinic and only pseudomonoclinic, although the structure that he suggested is realizable in the monoclinic space group $C2/m$ (C_{2h}^3), as Niggli himself pointed out. The conclusion that tenorite is in reality triclinic was based on the optical work of Kalkowsky, which has been discussed in the preceding section. The structure proposed by Niggli is not correct and is disproved by powder, rotation, and Weissenberg photographs, all of which contain diffraction lines or spots that could not be accounted for if Niggli's proposed structure were correct. Lack of sufficient resolution and of a sufficiently intense source of radiation prevented Niggli from recognizing the existence of a CuK_α line with $\sin\theta = 0.281$ and the corresponding CuK_β line with $\sin\theta = 0.253$, as a comparison of his table 5[2]) with our table VI readily shows; these lines are both sharp and amply intense to be unmistakable on our powder photographs taken with copper radiation and there are unmistakable lines of the same spacing on our powder photographs taken with molybdenum radiation. Additional conclusive evidence is furnished by the rotation and Weissenberg photographs described below, which contain many diffraction spots that could not be present if Niggli's proposed structure were correct. We have also calculated the intensities to be expected from Niggli's proposed structure and find that they do not agree with those observed by us. The positions of the copper atoms were correctly described by Niggli, however, and this is probably as much as could be expected from the meager data at his disposal. Thus Niggli[3]) himself wrote: "Das *Cu*-Gitter scheint mir endgültig bestimmt zu sein. Die Lage der *O*-Atome ist noch einer Nachprüfung zu unterwerfen, sobald die Gesetze der Reflexion besser bekannt sind."

In the present investigation it was found that the arrangement of the oxygen atoms is quite different from that suggested by Niggli and the relation of the oxygen atoms to the copper atoms is also different, the coordination number of the oxygen atoms with respect to the copper atoms being in reality four instead of six as assumed by Niggli.

Unit cell dimensions. The unit cell dimensions of the artificial single crystals were computed from measurements made on an excellent rotation photograph taken with copper radiation. The equator and first and second layer-lines were analyzed by means of Weissenberg photographs and thus the indices of each diffraction spot of these layer-lines were uniquely and rigorously established. In the computation of the unit cell dimensions only the measurements on the rotation photograph were used, however, since the accuracy of results obtained by combining measurements from the several Weissenberg films would have been no greater and probably would not have been quite as great. Moreover, the Weissenberg photographs were analyzed by the graphical construction of

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[1]) Niggli's *a*- and *c*-axes have been interchanged to correspond with the orientation used in the present investigation.

[2]) Op. cit., p. 271.

[3]) Op. cit., p. 292.

Schneider[1]), which is amply accurate for rigorous indexing of the Weissenberg photographs but which would yield slightly less accurate numerical values of the cell constants than the purely arithmetical method used in the computation of the unit cell dimensions from the measurements on the rotation photograph. Each unit cell dimension (a_0, b_0, c_0, and β) rests on the average of measurements of different spacings on the rotation photograph taken with copper radiation and was obtained from purely röntgenographic measurements. The values resulting are: $a_0 = 4.653$ Å, $b_0 = 3.410$ Å, $c_0 = 5.108$ Å, all ± 0.010 Å, $\beta = 99°29' \pm 20'$. In a preliminary report we published unit cell dimensions computed from measurements made on a rotation photograph of one of the artificial faceted crystals taken with molybdenum radiation; the values obtained with molybdenum radiation are: $a_0 = 4.66$ Å, $b_0 = 3.40$ Å, $c_0 = 5.09$ Å, all $\pm$ 0.02 Å, $\beta = 99°37' \pm 30'$, and are in satisfactory agreement with the later results obtained with copper radiation. The absolute value of b_0 was obtained from a powder photograph of a mixture of cupric oxide and sodium chloride taken with copper radiation, on which the line representing the second order reflection of (010) of cupric oxide was compared with nearby sharp lines of sodium chloride. The spacing of the plane, (010), of cupric oxide was then used to standardize the rotation photograph of the single crystal of artificial tenorite taken with copper radiation[2]). This crystal was acicular, being elongated parallel to the c-axis and was about 0.02 mm. in diameter and 1.1 mm. in length. The diameter was so small that no correction was necessary for the thickness of the crystal in the evaluation of the rotation photograph.

The reflections from the prisms, ($hk0$), appeared as single spots on the rotation film (Cu-radiation), and each of these spots was separated into four individual reflections by the translation of the Weissenberg camera parallel to the axis of rotation of the crystal. Observation that the two faces, $hk0$ and $h\bar{k}0$, have the same spacing would suffice to prove that the polar angle, $\nu\,(100 \wedge 010)$, is equal to 90°. One cannot say positively from the inspection of the film of any crystal, however, that the reflections of these two faces exactly superpose; one can only say that the centers of the spots cannot be separated more than a certain distance. On our film the separation of the $K\alpha_1$ reflections of 420 and $4\bar{2}0$ cannot be more than 0.1 mm., the radius of the camera being 35.0 mm. The

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[1]) Z. Kristallogr. 69 (1928) 41.

[2]) The same method was used in the analysis of the powder and rotation photographs taken with molybdenum radiation by means of which our earlier values of the unit cell dimensions were obtained.

maximum tolerance in the angle, $\nu = 90°$, is accordingly $\pm 7'$. Similarly the reflections from the pyramids and clinodomes of the upper termination appeared as single spots on the same rotation film, and each of these spots was separated into two individual reflections by the translation of the Weissenberg camera. Observation that the two faces, hkl and $h\bar{k}l$, have the same spacing, combined with the observation that the two faces, $hk0$ and $h\bar{k}0$, have the same spacing, would prove that the polar angle, $\lambda(001 \wedge 010)$, is equal to 90°. On our film the separation of the $K\alpha_1$ reflections of 131 and $1\bar{3}1$ cannot be more than 0.1 mm. The maximum tolerance in the angle, $\lambda = 90°$, set by these limits (in combination with the tolerance of $\pm 7'$ in the angle ν) is $\pm 18'$.

Determination of space group. The reflections with copper radiation found to be present in the equator and first and second layer-lines of the artificial single crystal elongated parallel to the c-axis (analyzed with

Table IV. Planar Spacings and Relative Intensities of the X-ray Diffraction Spots of Tenorite from a Rotation Photograph with *Cu*-radiation.

Rotation axis is c-axis (orientation of present authors).

Indices	Spacing (Calculated)	Relative Intensity		*CuK* Radiation2)	Indices	Spacing (Calculated)	Relative Intensity		*CuK* Radiation2)
		Observed1)	Calculated				Observed1)	Calculated	
110	2.737	m	7130	$\alpha_1 + \alpha_2$	131	1.069	m	4226	α_1
200	2.295	s	30009	$\alpha_1 + \alpha_2$	$\bar{3}31$	.914	m	4595	α_1
020	1.705	m	13880	α_1	$\bar{5}11$	.898	m	5752	α_1
310	1.396	w	659	α_1	331	.883	m	9563	α_1
220	1.369	s	24455	α_1	511	.850	m	9634	α_1
400	1.147	m	9577	α_1	$\bar{1}12$	1.952	m	1480	$\alpha_1 + \alpha_2$
420	.952	m	10372	α_1	$\bar{2}02$	1.855	s	24537	$\alpha_1 + \alpha_2$
510	.886	w	262	α_1	112	1.769	w	1085	$\alpha_1 + \alpha_2$
040	.853	m	6917	α_1	202	1.572	m	10558	α_1
240	.799	m	31919	α_1	022	1.412	m	13268	α_1
$\bar{1}11$	2.511	s	48013	$\alpha_1 + \alpha_2$	$\bar{3}12$	1.307	w	258	α_1
111	2.312	s	67035	$\alpha_1 + \alpha_2$	$\bar{2}22$	1.255	m	6686	α_1
021	1.615	w	543	α_1	222	1.156	m	5744	α_1
$\bar{3}11$	1.400	m	13061	α_1	$\bar{4}02$	1.116	w	2209	α_1
$\bar{2}21$	1.355	w	301	α_1	402	.985	w	2087	α_1
311	1.296	m	7169	α_1	$\bar{4}22$	.934	m	7310	α_1
221	1.289	w	250	α_1	422	.853	m	9454	α_1
$\bar{1}31$	1.087	m	8754	α_1					

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1) Denotation of symbols: *s*, strong; *m*, medium; *w*, weak.

2) The symbol, $\alpha_1 + \alpha_2$, denotes an unresolved spot resulting from α_1- and α_2-rays together; the symbol, α_1, denotes a spot resulting from α_1-rays alone.

Weissenberg photographs by the graphical construction of Schneider) are listed in table IV. The third layer-line of the rotation photograph with copper radiation and the entire rotation photograph taken with molybdenum radiation were analyzed by the graphical construction of Bernal[1]) with the help of the charts prepared by him. The powder photographs taken with molybdenum and with copper radiation were analyzed by the following method. From the unit cell dimensions obtained from the rotation photograph (copper radiation) all planar spacings existing in the crystalline substance and greater than 0.880 Å were computed[2]) and arranged in a column in descending order with the corresponding indices in a parallel column. The spacings observed on the powder photographs were compared with the computed spacings. Some of the observed lines could not be correlated with a single plane owing to the close succession of calculated spacings. The photograph taken with copper radiation was obtained without the use of a filter and thus presents additional complications on account of the presence of many beta lines. The presences and absences in all these films are listed in table V. In this table a + indicates that the plane gave an observable reflection; a 0 indicates that the plane was in a position to reflect and that no reflection of this spacing is present on the film; a + ? indicates that a line is present of approximately the spacing of the given plane and is probably due at least in part to the given plane although it might be ascribed to another plane or planes; a 0 ? indicates that a line is present of approximately the spacing of the given plane, which should not reflect, but the line can be ascribed to some other plane which should reflect if our structure be correct; lastly a blank space indicates that the plane was not in a position to reflect during the exposures. Thus it will be seen that planes having the following combinations of indices gave reflections, $g00$, $0g0$, $00g$, $0gu$, $0gg$, $g0g$, $uu0$, $gg0$, uuu, uug, ggu, ggg, where g denotes any even number and u denotes any odd number, and that no reflections appeared that would have to be ascribed to planes having the following combinations of indices, $u00$, $0u0$, $00u$, $0uu$, $0ug$, $u0u$, $u0g$, $g0u$, $ug0$, $gu0$, ugu, ugg, guu, gug, although representatives of each combination were in positions to reflect where they could not be masked by planes

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1) Proc. Roy. Soc. London (A) **113** (1926) 139.

2) By use of the properties of the reciprocal lattice it was readily possible to prove that all planes any index of which is higher than 5 have spacings less than 0.880. The spacings of all other planes were either computed or proved to be less than the spacing of some plane one index of which is higher than 5 or less than the spacing of some plane that had been computed and found to be less than 0.880.

Table V. Presences and Absences of Diffraction Spots from all Atomic Planes of Tenorite the Spacings of which are greater than 0.880 Å.

Indices	Spacing	Presence or absence demanded by structure of G.T., E.P. and C.J.K.	Actual presence or absence1)				Calculated intensities of diffraction lines of *Mo*-powder spectrum	Indices	Spacing	Presence or absence demanded by structure of G.T., E.P. and C.J.K.	Actual presence or absence1)				Calculated intensities of diffraction lines of *Mo*-powder spectrum
			Cu-P	*Cu-RW*	*Mo-P*	*Mo-R*					*Cu-P*	*Cu-RW*	*Mo-P*	*Mo-R*	
001	5.038	0	0		0	0	0	$\bar{3}02$	1.415	0	0?	0	0?	0?	0
100	4.590	0	0	0	0	0	0	022	1.412	+	+?	+	+?	+?	75442
$\bar{1}01$	3.711	0	0	0	0	0	0	301	1.401	0	0?	0	0?	0?	0
010	3.410	0	0	0	0	0	0	$\bar{3}11$	1.400	+	+?	+	+?	+?	74397
101	3.145	0	0	0	0	0	0	310	1.396	+	+?	+	0	+?	1879
011	2.824	0	0	0	0	0	0	$\bar{1}22$	1.386	0	0	0	0	0	0
110	2.737	+	+	+	+	+	11287	113	1.373	+	+?	+?	+?	+	47039
002	2.519	+	+?		+?	+	57423	220	1.369	+	+?	+	+?	+?	69947
$\bar{1}11$	2.511	+	+?	+	+?	+	154537	$\bar{2}21$	1.355	+	0	+	0	0	1727
$\bar{1}02$	2.380	0	0	0	0	0	0	$\bar{2}13$	1.355	0	0	0?	0	0?	0
111	2.312	+	+?	+	+?	+	219713	122	1.316	0	0	0	0	0	0
200	2.295	+	+?	+	+?	+	49263	$\bar{3}12$	1.307	+	+?	+	+?	0	1485
$\bar{2}01$	2.232	0	0	0	0	0	0	311	1.296	+	+?	+	+?	+?	41213
102	2.069	0	0	0	0	0	0	221	1.289	+	+?	+	+?	+?	1439
012	2.026	0	0	0	0	0	0	$\bar{1}04$	1.269	0	0		0		0
201	1.970	0	0	0	0	0	0	004	1.260	+	+?		+?		33503
$\bar{1}12$	1.952	+	+	+	0	0	5077	203	1.260	0	0?	0	0?	0	0
210	1.904	0	0	0	0	0	0	$\bar{2}22$	1.255	+	+?	+	+?	+	38364
$\bar{2}11$	1.867	0	0	0	0	0	0	$\bar{3}03$	1.237	0	0	0	0	0	0
$\bar{2}02$	1.855	+	+	+	+	+	85468	302	1.221	0	0	0	0	0	0
112	1.769	+	0	+	0	0	3837	023	1.197	+	0	0	0	0	1105
211	1.706	0	0?	0	0?	0	0	$\bar{1}23$	1.192	0	0?	0	0?	0	0
020	1.705	+	+?	+	+?	+	37270	$\bar{2}04$	1.190	+	+?		+?	+?	13695
003	1.679	0	0		0		0	$\bar{1}14$	1.190	+	+?		+?	+?	1069
$\bar{1}03$	1.668	0	0?		0		0	213	1.182	0	0?	0?	0	0?	0
$\bar{2}12$	1.630	0	0	0	0	0	0	014	1.182	0	0?		0	0	0
021	1.615	+	0	+	+	0	2971	104	1.167	0	0?		0	0	0
120	1.598	0	0	0	0	0	0	$\bar{3}13$	1.163	+	+?	+?	+?	+?	32224
202	1.572	+	+	+	+	+	58231	$\bar{4}01$	1.161	0	0?	0	0?	0	0
$\bar{1}21$	1.549	0	0?	0	0	0	0	222	1.156	+	+?	+	+?	+?	31967
$\bar{3}01$	1.536	0	0	0	0	0	0	312	1.150	+	+?	0	+?	+?	951
300	1.530	0	0	0	0	0	0	400	1.147	+	+?	+	+?	+?	26513

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1) Denotation of symbols in heading: *Cu—P* denotes powder photograph taken with copper *K*-radiation; *Cu—RW* denotes rotation and Weissenberg photographs taken with copper *K*-radiation (the equator, first, and second layer-lines were analyzed by Weissenberg photographs and all spots on them were uniquely indexed; the third layer-line of this rotation photograph was analyzed only by the graphical construction of Bernal and none of its spots were uniquely indexed);

Table V (continuation).

Indices	Spacing	Presence or absence demanded by structure of G. T., E. P. and C. J. K.	Actual presence or absence				Calculated intensities of diffraction lines of *Mo*-powder spectrum	Indices	Spacing	Presence or absence demanded by structure of G. T., E. P. and C. J. K.	Actual presence or absence				Calculated intensities of diffraction lines of *Mo*-powder spectrum
			Cu-P	*Cu-RW*	*Mo-P*	*Mo-R*					*Cu-P*	*Cu-RW*	*Mo-P*	*Mo-R*	
013	1.507	0	0?		0	0?	0	$\bar{3}21$	1.141	0	0	0	0	0	0
121	1.499	0	0?	0	0?	0	0	320	1.139	0	0	0	0	0?	0
103	1.499	0	0?		0?	0?	0	030	1.137	0	0	0	0	0?	0
$\bar{1}13$	1.499	+	+?		+?	+?	87192	123	1.126	0	0	0	0	0	0
$\bar{2}03$	1.476	0	0		0	0	0	$\bar{2}14$	1.124	0	0?		0?	0	0
212	1.428	0	0	0	0	0?	0	$\bar{2}23$	1.116	+	+?	0	+?	0	864
$\bar{4}02$	1.116	+	+?	+	+?	0	11941	$\bar{2}24$	.976	+	+?		+?	+?	29149
031	1.109	0	0?	0	0	0	0	$\bar{2}32$	.969	0	0?	0	0	0	0
114	1.104	+	0		0	0	817	015	.966	0	0?		0		0
130	1.103	+	0	0	0	0	0^+	124	.963	0	0?		0?	0	0
$\bar{4}11$	1.099	0	0	0	0	0?	0	$\bar{4}21$	.960	+	+?	0	+?	0	485
$\bar{3}22$	1.089	0	0?	0	0?	0	0	420	.952	+	+?	+	+?	+	19817
$\bar{1}31$	1.087	+	+?	+	+?	+?	45899	105	.952	0	0?		0?		0
410	1.087	0	0?	0	0?	0	0	412	.946	0	0?	0	0	0	0
321	1.082	0	0?	0	0?	0?	0	$\bar{2}15$	.946	0	0?		0		0
401	1.081	0	0?	0	0	0?	0	033	.941	0	0?	0?	0?	0?	0
131	1.069	+	+?	+	+?	+?	21644	$\bar{1}33$	.939	+	+?	+?	+?	+?	15846
$\bar{3}04$	1.062	0	0?		0?	0	0	$\bar{4}22$	.934	+	+?	+	+?	+?	25860
$\bar{4}12$	1.060	0	0?	0	0	0	0	$\bar{5}01$	.930	0	0?	0	0	0	0
303	1.048	0	0?	0	0?	0	0	$\bar{4}04$	.928	+	+?		+?	+	14709
032	1.036	0	0?	0	0?	0	0	232	.921	0	0?	0	0?	0?	0
204	1.035	+	+?		+?	+	10044	500	.918	0	0?	0	0?	0	0
411	1.030	0	0?	0	0	0	0	115	.917	+	+?		+?	+?	24666
$\bar{4}03$	1.030	0	0?	0	0	0	0	$\bar{3}31$	.914	+	+?	+	+?	0	14741
$\bar{1}32$	1.026	+	0	0	0	0	0^+	$\bar{3}05$	.914	0	0?		0?	0?	0
$\bar{1}05$	1.020	0	0?		0?		0	421	.913	+	+?	0	+?	0	407
230	1.018	0	0?	0	0?	0	0	330	.912	+	+?	0	+?	0	0^+
$\bar{1}24$	1.018	0	0?		0?	0?	0	$\bar{5}02$	.912	0	0?	0	0?	0?	0
$\bar{3}14$	1.014	+	+?		+?	+?	578	133	.906	+	+?		+?	+?	27463

Mo—P denotes powder photograph taken with molybdenum *K*-radiation; *Mo—R* denotes rotation photograph taken with molybdenum *K*-radiation.

Denotation of symbols in table: + indicates that the plane gave an observable reflection; 0 indicates that the plane was in a position to reflect and that no reflection of this spacing is present on the film; + ? indicates that a line is present of approximately the spacing of the given plane and is probably due at least in part to the given plane although it might be ascribed to another plane or planes; 0 ? indicates that a line is present of approximately the spacing of the given plane, which should not reflect, but the line can be ascribed to some other plane which should reflect if our structure be correct; a blank space indicates that the plane was not in a position to reflect during the exposures.

Table V (continuation).

Indices	Spacing	Presence or absence demanded by structure of C. T., E. P. and C. J. K.	Actual presence ar absence				Calculated intensities of diffraction lines of *Mo*-powder spectrum	Indices	Spacing	Presence or absence demanded by structure of G. T., E. P. and C. J. K.	Actual presence or absence				Calculated intensities of diffraction lines of *Mo*-powder spectrum
			Cu-P	*Cu-RW*	*Mo-P*	*Mo-R*					*Cu-P*	*Cu-RW*	*Mo-P*	*Mo-R*	
$\bar{2}31$	1.013	0	0?	0	0?	0	0	304	.902	0	0?		0?	0	0
223	1.013	+	+?	+?	+?	+?	588	$\bar{2}33$	.901	0	0?		0?	0?	0
024	1.013	+	+?		+?	+?	23208	$\bar{3}24$	.901	0	0?		0?	0	0
005	1.008	0	0?		0?		0	$\bar{5}11$	.898	+	+?	+	+?	0	16842
313	1.002	+	+?	+?	+?	+?	31412	$\bar{4}14$	.895	0	0?		0	0?	0
$\bar{3}23$	1.001	0	0?	0?	0?	0?	0	323	.893	0	0		0?	0?	0
132	.996	+	0	0	0	0	0^{+}	$\bar{3}32$	.886	+	+?	0	+?	0	0^{+}
322	.993	0	0?	0	0	0	0	510	.886	+	+?	+	+?	0	357
214	.990	0	0?		0	0?	0	224	.884	+	+?		+?	+?	22175
$\bar{4}13$	.986	0	0?	0	0	0?	0	331	.883	+	+?	+	+?	+?	25435
402	.985	+	+?	+	+?	0	8928	$\bar{3}15$	.882	+	+?		+?	+	22075
231	.984	0	0?	0	0	0	0	403	.882	0	0?		0?	0	0
$\bar{2}05$	.984	0	0?		0?		0	$\bar{4}23$	.881	+	+?		+?	0	358
$\bar{1}15$	.977	+	+?		+?		21078	$\bar{5}12$	.881	+	+?	0	+?	0	351

permitted to reflect if our structure be correct. The extinctions are the theoretical extinctions of the space groups, $C2/c$ (C_{2h}^{6}) and Cc (C_{s}^{4}), the theoretical extinctions of these two space groups being identical. The crystal habit indicated by Jenzsch's and Story-Maskelyne's drawings of crystals measured by them on the reflection goniometer is that of the holohedral class of the monoclinic system. The crystal[1]) measured by us on the reflection goniometer (the same crystal was also investigated by the rotation and Weissenberg methods) exhibited four prism faces of approximately equal extent and of similar appearance all yielding fair signals on the reflection goniometer, and is thus holohedral in habit although no terminal faces could be observed on it.[2]) Of the two alternatives crystal habit alone therefore points strongly to the space group, $C2/c$ (C_{2h}^{6}); however, in the search for the atomic arrangement exhaustive consideration was also given to the possibilities in the space group, Cc (C_{s}^{4}).

Atomic arrangement. The measured density of tenorite crystals is 6.45 according to Th. Richter.[3]) Ruer and Kuschmann[4]) determined

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1) Prepared by recrystallization in molten sodium hydroxide.

2) This crystal tapered off to a point. Other crystals from the same preparation exhibited terminal faces in addition to prism faces but the terminal faces were too small to be identified.

3) Poggendorffs Ann. Phys. u. Chem. **107** (1859) 648.

4) Z. anorg. Chem. **154** (1926) 74, 75.

the density of artificial cupric oxide to be 6.32. The latter value is undoubtedly too low owing to the fine-grained character of the artificial product. The number of molecules in the unit cell can only be four, the density calculated from the X-ray measurements being accordingly 6.569.

In the space group, $C2/c$ (C_{2h}^6), there are five groups of four equivalent positions: (a) $0, 0, 0$; $0, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; (b) $0, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; (c) $\frac{1}{4}, \frac{1}{4}, 0$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$; $\frac{3}{4}, \frac{3}{4}, 0$; (d) $\frac{3}{4}, \frac{3}{4}, \frac{1}{2}$; $\frac{1}{4}, \frac{3}{4}, 0$; $\frac{3}{4}, \frac{1}{4}, 0$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; (e) $0, n, \frac{3}{4}$; $0, \bar{n}, \frac{1}{4}$; $\frac{1}{2}, n+\frac{1}{2}, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2}-n, \frac{1}{4}$,[1] of which (a), (b), (c), (d) consist of symmetry centers, and (e) consists of points lying on symmetry axes. The following combinations must therefore be considered.

I. All possible arrangements of copper and oxygen atoms in symmetry centers (i. e. all possible combinations of (a), (b), (c), (d)) can be eliminated at once since they all require the intensity of the reflection of (020) to be stronger than that of (202), whereas the opposite is actually observed.

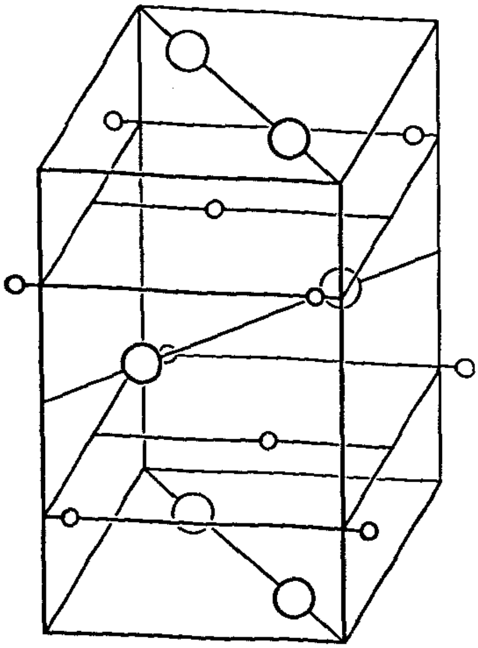

Fig. 1. Arrangement of the copper and oxygen atoms in tenorite (cupric oxide). The parallelepiped represented by the outside lines is the unit cell. Large circles represent copper atoms; small circles represent oxygen atoms.

II. All possible arrangements of copper and oxygen atoms on symmetry axes (i. e. both copper and oxygen atoms situated in (e) but with different parameter values) can be eliminated since they require that the reflections of ($\bar{1}31$) and (131) (immediately adjacent lines on the powder photograph taken with molybdenum radiation) shall be so nearly equal, for any values of the parameters whatsoever, as to be indistinguishable on the photographic film; actually the intensity of the reflection from ($\bar{1}31$) is at least twice that of the reflection from (131). Moreover, all combinations of parameter values that lead to calculated intensities anything like those observed require an improbably close approach of oxygen and copper atoms.

III. Arrangements of copper atoms on symmetry axes and oxygen atoms on symmetry centers may be discussed in two parts, as follows. 1. All arrangements of copper atoms in (e) and oxygen atoms in either (a) or (b) can be eliminated because they require very nearly equal intensities for ($\bar{1}31$) and (131), which is contrary to fact. 2. All arrangements of copper atoms in (e) and oxygen atoms in (c) or (d)

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[1] The groups of equivalent points are designated by the same letters used by **Wyckoff**, but are here referred to axes oriented similarly to those of **Niggli** in order to facilitate the comparison of the observed extinctions with those listed in **Herrmann's** "Röntgenographische Auslöschungstabellen", in which the orientations of **Niggli** are followed.

can be eliminated because they require a much lower intensity for (110) and a much higher intensity for (020) than is actually observed.

IV. Arrangements of oxygen atoms on symmetry axes and copper atoms on symmetry centers may be discussed in three parts, as follows. 1. Arrangements of oxygen atoms in (e) and copper atoms in (a) or (b) can be eliminated because they require a fairly strong reflection from (130), whereas

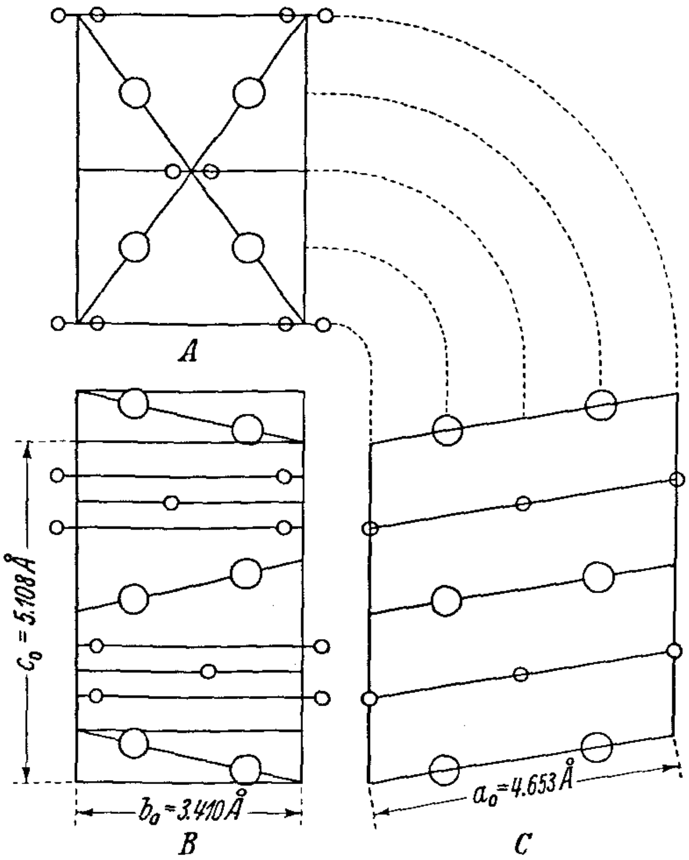

Fig. 2. Orthographic projections of the unit cell of tenorite. A. Top view. B. Front view. C. Side view. Large circles—copper atoms. Small circles—oxygen atoms.

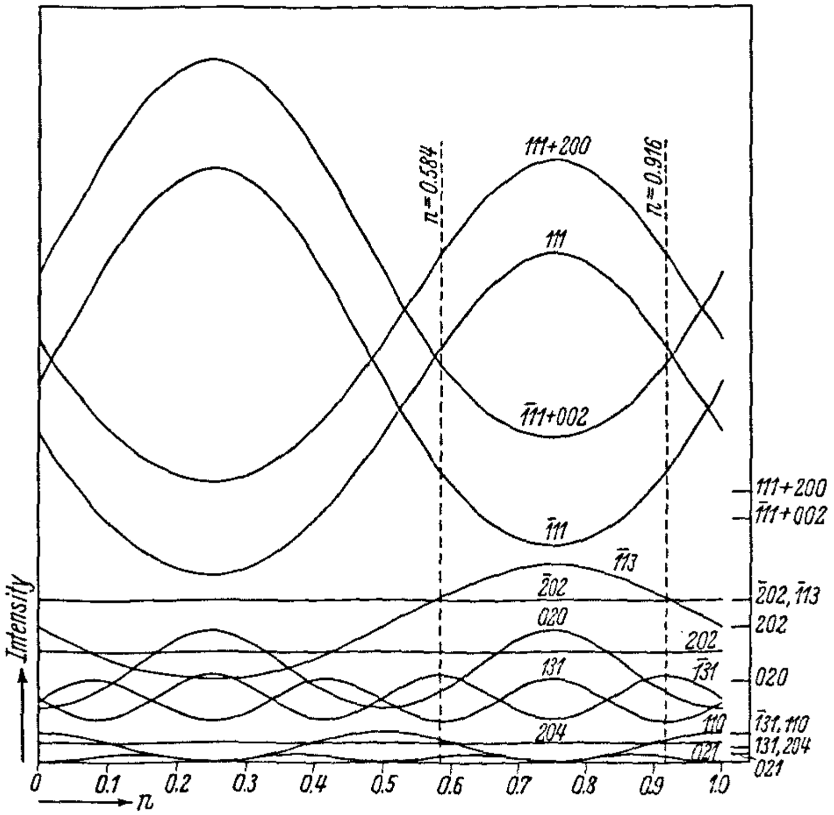

Fig. 3. The effect of the parameter value on the calculated intensities of the principal lines of tenorite. The observed intensities in the powder photograph taken with molybdenum K-radiation are indicated along the right-hand vertical margin. The two possible values of the parameter determined by these curves are indicated by the vertical lines; the two values of the parameter result in the same structure.

actually no reflection can be obtained from this plane even with prolonged and powerful radiation when the crystal is in the appropriate position to reflect. 2. Arrangements of oxygen atoms in (e) and copper atoms in (c) or (d) remain to be considered. If the oxygens are placed in (e) and the coppers are placed in (c), there are two values of the oxygen parameter n_O, namely, 0.916 and 0.584, each with a tolerance of about 0.010, that yield identical values of all the calculated intensities and that are at the same time in agreement with all the observed intensities, as is shown by fig. 3 and tables IV and VI.

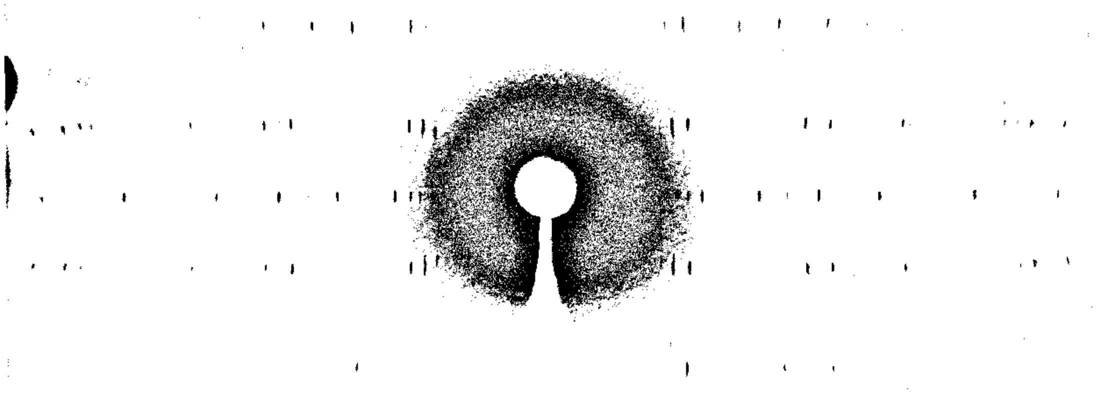

Fig. 4.

The intensities were calculated from the formula

$$I = \frac{1 + \cos^2 2\theta}{\sin 2\theta} jF^2$$

with use of the atomic F-values of James and Brindley[1]) for atomic copper and atomic oxygen. The calculated intensities would not be appreciably different, in comparison with the observed intensities, if the F-values of James and Brindley for cupric ions and oxygen ions were used instead.

The two arrangements furnished by the two different values of the parameter, although differently placed with respect to the origin, can readily be superposed by a translation of $\tau_a - \tau_c$ of the second arrangement and are therefore identical. 3. If the oxygens are placed in (e) and the coppers in (d) a case arises that can be reduced to case IV. 2. by a translation of the new arrangement of τ_c; n'_O is thus equal to $-n'_O$, that is n'_O equals 0.084 or 0.416.

In the space group, Cc (C_s^4), there is only one group of equivalent positions and it consists of the four general positions: (a) m, n, p; $m, \bar{n}, p + \frac{1}{2}$; $m + \frac{1}{2}, n + \frac{1}{2}, p$; $m + \frac{1}{2}, \frac{1}{2} - n, p + \frac{1}{2}$. We must therefore consider arrangements of copper atoms and oxygen atoms each in (a) but having different values of the parameters.

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[1]) Phil. Mag. (7) 12 (1931) 104.

The only symmetry elements in this space group are glide symmetry planes and the origin may be taken anywhere in one of the glide symmetry planes with the glide component, $c/2$. Thus the m- and p-parameters of the copper atoms can be assigned the values $m_{Cu} = \frac{1}{4}$ and $p_{Cu} = 0$ without loss of generality. The m- and p-parameters of the oxygen atoms must then be determined by consideration of the intensities. In order to obtain a calculated ratio of the intensity of (200) to that of ($\bar{2}02$) as low as that actually observed on the Cu-radiation rotation film m_O must lie near 0 or $\frac{1}{2}$. The ratios of the observed intensity of (400) to that of ($\bar{4}02$) and of the observed intensity of (400) to that of (402) on the same rotation film lead to the conclusion that m_O must lie near 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ and restrict the ranges about these values very closely. The ratios of the observed intensity of (400) to that of ($\bar{4}02$) and of the observed intensity of (400) to that of (402) can only be accounted for if the full (or nearly the full) scattering power of the four oxygen atoms is added to the full scattering power of the four copper atoms in the case of the reflection (400) and if the full (or nearly the full) scattering power of the four oxygen atoms is subtracted from the full scattering power of the four copper atoms in the case of the reflection ($\bar{4}02$) and also the reflection (402). These two ratios of observed intensities ((400) to ($\bar{4}02$) and (400) to (402)) likewise restrict the value of p_O to narrow ranges about $\frac{1}{4}$ or $\frac{3}{4}$. Numerical analysis of the data cited shows that $m_O = 0$ or $\frac{1}{2}$ each with a tolerance of about ± 0.01 and $p_O = \frac{1}{4}$ or $\frac{3}{4}$ each with a tolerance of about ± 0.04.

Finally the parameters along the axis perpendicular to the glide symmetry plane (that is, the b-axis) are to be determined. The fact that the plane (130) gave no observable reflection on the rotation films although it was in a position to reflect restricts the value of n_{Cu} to narrow ranges about $\frac{1}{12}$, $\frac{1}{4}$, $\frac{3}{4}$, or $\frac{11}{12}$, and the low observed intensity of (110) shows that the first and fourth of these alternatives are impossible. Numerical analysis of the data cited shows that $n_{Cu} = \frac{1}{4}$ or $\frac{3}{4}$ each with a tolerance of about ± 0.01.

The determination of the n-parameter of the oxygen atoms then follows in a manner similar to that already explained in the discussion of possible arrangements in the space group, $C2/c$ (C_{2h}^6). There are eight combinations of the values determined for the parameters, m_{Cu}, n_{Cu}, p_{Cu}, m_O, p_O, in the space group, Cc, and the determination of the parameter, n_O, will therefore be carried out in eight cases, in each of which it will be found, however, that the same structure must result. The eight cases are as follows:

V. 1. First combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{1}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = 0 \pm 0.01$, $p_O = \frac{3}{4} \pm 0.04$. This combination has already been discussed as case IV. 2. under the space group, $C2/c$; there are only two narrow ranges of values of n_O that result in calculated intensities agreeing with the observed intensities; they are n_O equals approximately 0.916 or 0.584. And it has already been shown under the space group, $C2/c$, that the same structure results no matter which of these values be assigned to n_O in this case.

V. 2. Second combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{1}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = 0 \pm 0.01$, $p_O = \frac{1}{4} \pm 0.04$. The oxygen parameter to be determined in this case is designated n_O^{II}; replacing n_O^{II} by a new variable, $-n_O$, we reduce the problem to case V. 1. in which the possible values of n_O have already been found to be 0.916 and 0.584; hence n_O^{II} equals approximately 0.084 or 0.416.

Table VI. Planar Spacings and Relative Intensities of the X-ray Diffraction Lines of Tenorite from Powder Spectra with *Mo*- and *Cu*-radiation.

Molybdenum radiation (filtered)

Sin θ measured	Spacing measured		Indices		Relative intensity	
	$\frac{d}{n}(\alpha)$	$\frac{d}{n}(\beta)$	α lines	β lines	observed	calculated (α lines only)
.42679		2.49		111, 002	½	
.42956	2.74		110		1	11287
.43760		2.29		111, 200	½	
.44143	2.51		$\bar{1}$11, 002		9	211960
.45435	2.30		111, 200		10	268976
.19137	1.855		$\bar{2}$02		6	85468
.20858	1.702		020		3	37270
.21968	1.616		021		¼	2971
.22525	1.576		202		5	58231
.23858	1.498		$\bar{1}$13		6	87192
.25267	1.405		$\bar{3}$11, 022		7	149839
.25912	1.370		220, 113		7	116986
.27371	1.297		311, $\bar{3}$12, 221		3	44137
.28242	1.257		$\bar{2}$22, 004		5	71867
.29857	1.189		$\bar{2}$04, $\bar{1}$14		1	14764
.30683	1.157		400, 222, $\bar{3}$13, 312		2 Very broad line	91655
.31753	1.118		$\bar{4}$02, $\bar{2}$23		½	12805
.32659	1.087		$\bar{1}$31		1	45899
.33147	1.071		131		½	21644
.34135	1.040		204		½	10044
.34838	1.019		024, 223		½	23796
.35288	1.006		313		½	31412
.36336	0.977		402, $\bar{2}$24, $\bar{1}$15		2	59155
.37134	0.956		420, $\bar{4}$21		½	20302

Copper radiation (not filtered)

Sin θ measured	Spacing measured		Indices		Relative intensity	
	$\frac{d}{n}(\alpha)$	$\frac{d}{n}(\beta)$	α lines	β lines	observed	calculated (α lines only)
.25332		2.742		110	1	
.27610		2.516		$\bar{1}$11, 002	3	
.28114	2.737		110		2	4753
.30038		2.313		111, 200	2	
.30622	2.513		$\bar{1}$11, 002		10	87821
.33357	2.307		111, 200		9	109386
.35492		1.957		$\bar{1}$12	½	
.37446		1.855		$\bar{2}$02	2	
.39385	1.954		$\bar{1}$12		¾	1974
.41544	1.852		$\bar{2}$02		6	32716
.44152		1.573		202	1	
.45170	1.704		020		2	13880
.46414		1.497		$\bar{1}$13	1	
.48875	1.575		202		3	21115
.49560		1.402		$\bar{3}$11, 310	¾	
.50695		1.370		220, 113	¾	
.51297	1.500		$\bar{1}$13		5	31151
.53458		1.300		311, $\bar{3}$12, 221	½	
.54562	1.411		022		1	26536
.54928	1.401		$\bar{3}$11, 310		3	26781
.56165	1.370		220, 113		5	40908
.59306	1.298		311, $\bar{3}$12, 221		2	15356
.61191	1.258		004, $\bar{2}$22		4	25045
.63719		1.090		$\bar{1}$31	¼ Is this a line?	

.37806	0.939		$\bar{4}22$, $\bar{1}33$		1	44706
.38545	0.921		$\bar{3}31$, 115, $\bar{4}04$, 421, 330		$\frac{1}{2}$	54523
.39227	0.905		133, $\bar{5}11$		$\frac{1}{2}$	44305
.40113	0.885		$\bar{3}15$, 331, 224, 332, 510, $\bar{4}23$, $\bar{5}12$		2	70751

.64794	1.488	1.072	$\bar{2}04$, $\bar{1}14$	131	1	
.66179	1.163		$\bar{3}13$, 222		2	23024
.66962	1.149	1.037	400, 312	204	1	
.68951	1.116		$\bar{4}02$, $\bar{2}23$		1	4738
.70890	1.086	0.980	$\bar{1}31$	$\bar{2}24$, $\bar{1}15$	2	
.71931	1.070	0.966	131	$\bar{4}21$	$\frac{1}{2}$	
.72896		0.953		420	$\frac{1}{4}$ Is this a line?	
.74317	1.036	0.935	204	$\bar{4}22$	1	
.75933	1.014	0.915	024, 223	115, $\bar{3}31$, 330, 421	2	
.76724	1.003	0.905	313	133	2	
.77889	0.988		402		$\frac{1}{2}$	4173
.78813	0.976	0.881	$\bar{2}24$, $\bar{1}15$	224, 331, $\bar{4}23$, $\bar{3}15$, $\bar{5}12$	3	
.79667	0.966		$\bar{4}21$		$\frac{1}{4}$ Is this a line?	247
.80712	0.954		420		1	10372
.81480	0.945	0.853	$\bar{1}33$	?	$<\frac{1}{4}$ Is this a line?	
.82233	0.936	0.845	$\bar{4}22$	?	2	
.82875	0.929	0.838	$\bar{4}04$	?	$\frac{3}{4}$	
.83984	0.916		115, $\bar{3}31$, 330, 421		2	
.84967	0.906	0.818	133	?	$\frac{3}{4}$	
.85516	0.900	0.812	$\bar{5}11$	?	$\frac{3}{4}$	
.86976	0.885	0.799	224, 331, $\bar{4}23$, $\bar{3}15$, $\bar{5}12$, $\bar{3}32$, 510	?	4	
.90062	0.855				3	
.91386	0.842				2	
.92048	0.836				2	
.94179	0.817				1	
.95056	0.810				$\frac{3}{4}$	
.96108	0.801				1	

V. 3. Third combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{1}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = \frac{1}{2} \pm 0.01$, $p_O = \frac{3}{4} \pm 0.04$. The oxygen parameter to be determined in this case is designated n_O^{III}; replacing n_O^{III} by a new variable, $\frac{1}{2} + n_O$, we reduce the problem to case V. 1. in which the possible values of n_O have already been found to be 0.916 and 0.584; hence n_O^{III} equals approximately 0.416 or 0.084.

V. 4. Fourth combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{1}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = \frac{1}{2} \pm 0.01$, $p_O = \frac{1}{4} \pm 0.04$. The oxygen parameter to be determined in this case is designated n_O^{IV}; replacing n_O^{IV} by a new variable, $\frac{1}{2} - n_O$, we reduce the problem to case V. 1. in which the possible values of n_O have already been found to be 0.916 and 0.584; hence n_O^{IV} equals approximately 0.584 or 0.916.

V. 5. Fifth combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{3}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = 0 \pm 0.01$, $p_O = \frac{3}{4} \pm 0.04$. This combination has already been discussed as case IV. 3. under the space group, $C2/c$; there are two narrow ranges of values of the parameter, n_O^V, that result in calculated intensities agreeing with the observed intensities; they are n_O^V equals approximately 0.084 or 0.416. And it has already been shown under the space group, $C2/c$, that the same structure results no matter which of these values be assigned to n_O^V in this case; this structure is moreover identical with that of case IV. 2.

V. 6. Sixth combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{3}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = 0 \pm 0.01$ $p_O = \frac{1}{4} \pm 0.04$. The oxygen parameter to be determined in this case is designated n_O^{VI}; replacing n_O^{VI} by a new variable, $-n_O^V$, we reduce the problem to case V. 5. in which the possible values of n_O^{VI} have already been found to be 0.084 and 0.416; hence n_O^{VI} equals approximately 0.916 or 0.584.

V. 7. Seventh combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{3}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = \frac{1}{2} \pm 0.01$, $p_O = \frac{3}{4} \pm 0.04$. The oxygen parameter to be determined in this case is designated n_O^{VII}; replacing n_O^{VII} by a new variable, $\frac{1}{2} + n_O^V$, we reduce the problem to case V. 5. in which the possible values of n_O^V have already been found to be 0.084 and 0.416; hence n_O^{VII} equals approximately 0.584 or 0.916.

V. 8. Eighth combination: $m_{Cu} = \frac{1}{4}$, $n_{Cu} = \frac{3}{4} \pm 0.01$, $p_{Cu} = 0$, $m_O = \frac{1}{2} \pm 0.01$, $p_O = \frac{1}{4} \pm 0.04$. The oxygen parameter to be determined in this case is designated n_O^{VIII}; replacing n_O^{VIII} by a new variable, $\frac{1}{2} - n_O^V$, we reduce the problem to case V. 5. in which the possible values of n_O^V have already been found to be 0.084 and 0.416; hence n_O^{VIII} equals approximately 0.416 or 0.084.

Thus by means of the intensities alone all possible arrangements in the space groups, $C2/c$ and Cc, have been excluded except one.[1] Except for possible very slight displacements from the positions given too small to affect the intensities visibly, this arrangement has the sym-

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[1] Such exceptions to the usual application of the theory of space groups as occur in the cases of compounds with variate atom equipoints or rotating groups are very improbable in the case of tenorite. Variate atom distribution of the four copper atoms and four oxygen atoms in the eight general positions of $C2/c$ is definitely excluded by the observed intensities of (110) and (130).

metry of the space group, $C2/c$, and the positions of the atoms are special positions of this space group.

The atoms are arranged in a four coordination, each oxygen being surrounded at approximately equal distances by four copper atoms on the corners of a non-equilateral tetrahedron, and each copper atom being surrounded at approximately equal distances by four oxygens lying in a plane at the corners of a rectangle. The interatomic distance $Cu—O$ is 1.95 Å, a value in good agreement with the radii predicted by M. L. Huggins¹) for copper and oxygen in a "tetrahedral" crystal in which the atoms are joined by electron-pair bonds. The radii predicted by Huggins are: *Cu*, 1.35 Å, and *O*, 0.66 Å; the interatomic distance $Cu—O$ would be accordingly 2.01 Å. Moreover, the slight difference between our observed and Huggins's calculated value is in line with previous results reported by Huggins. Thus he writes: "The observed distances in *BeO*, *AlN*, and *SiC* indicate a decrease from the calculated values of about 0.05 to 0.10 Å, due probably to small kernel repulsion, if the more negative atom is carbon, nitrogen, oxygen, or fluorine and the more positive atom is of an element in the first or second row of the Periodic Table." A decision as to the nature of the binding in tenorite is not possible from the observed interatomic distance alone, however, since this distance is also in good agreement with that obtained from V. M. Goldschmidt's²) curves of ionic radii, namely, 2.01 Å, on the assumption that the crystal is composed of cupric and oxygen ions in a four coordination³). Some light is thrown on this problem by the fact that the alternate tetrahedra of copper atoms in the structure are empty, but are of the same size and shape as those containing an oxygen atom at the center. Some expansion of the empty tetrahedra as compared with those containing an oxygen atom at the center would be expected if the binding were purely ionic.

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1) Chem. Rev. **10** (1932) 440.

2) Trans. Faraday Soc. **25** (1929) 258.

3) Goldschmidt's value for the radius of divalent negative oxygen in a six coordination is that of Wasastjerna, namely, 1.32 Å. Goldschmidt does not plot any value for the radius of divalent positive copper on his chart of ionic radii versus atomic number, but he does plot values for the radii of divalent positive nickel and zinc in a six coordination and draws a dotted curve connecting them. This dotted curve indicates a radius of 0.80 Å for divalent positive copper in a six coordination. To obtain the value of the corresponding interionic distance, $Cu^{2+}—O^{2-}$, in a four coordination we have multiplied that in a six coordination, $1.32 + 0.80$, by 0.95 (cf. Huggins, op. cit., pp. 441, 443).

Summary.

The monoclinic symmetry of tenorite was proved by means of X-ray analysis and independently by optical measurements and was confirmed by careful study of the cleavages. The unit cell of tenorite has the following dimensions: $a_0 = 4.653$ Å, $b_0 = 3.410$ Å, $c_0 = 5.108$ Å, all ± 0.010 Å, $\beta = 99°29' \pm 20'$, leading to the axial ratio: $a:b:c = 1.365:1:1.498$; the unit cell contains four "molecules" of CuO. The X-ray density is 6.569. The structure is isomorphous with the space group $C2/c$ (C_{2h}^6) and the four copper atoms occupy the positions, $\frac{1}{4}, \frac{1}{4}, 0$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$; $\frac{3}{4}, \frac{3}{4}, 0$ and the four oxygen atoms the positions, $0, n, \frac{3}{4}$; $0, \bar{n}, \frac{1}{4}$; $\frac{1}{2}, n+\frac{1}{2}, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2}-n, \frac{1}{4}$, where $n = 0.916$ or 0.584, these two values of the parameter leading to the same structure.

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