

CRYSTALLOGRAPHY AND COMPOSITION OF CREDNERITE

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ABSTRACT

Crednerite from the Mendip Hills, Somerset, is monoclinic, with unit cell dimensions a 5.58, b 2.87, c 5.87, Å, β 104.0°, and space group $C2/m$, $C2$ or Cm . The composition of CuMn_2O_4 , from the chemical analysis by Mountain, gives an irrational unit cell content for the measured density of 5.03 gm./cc. Above 1100° C. in air copper manganese oxide mixtures form crednerite together with copper hausmannite or cuprite, depending on the overall composition. The synthetic crednerite is of composition $\text{Cu}_2\text{Mn}_2\text{O}_6$, comparable to crednerite from Friedrichroda.

Crednerite was first found as foliated crystals at Friedrichroda, Thuringia, from where it was described by Credner (1847). A perfect basal cleavage with two less perfect cleavages oblique to it indicated a possible monoclinic symmetry, and Rammelsberg (1849) deduced the chemical formula of $3\text{CuO} \cdot 2\text{Mn}_2\text{O}_3$ from analyses and gave to this mineral the name crednerite. Meanwhile Hausmann (1847) had briefly described it in Vol. 2 of his "Handbuch der Mineralogie" (p. 1582) under the name mangankupferoxyd.

No other occurrence of crednerite was described until 1923, when Spencer and Mountain (1923) identified it as plates up to $10 \times 10 \times 1$ mm. from a locality at the Higher Pitts Farm, Priddy, Mendip Hills, Somerset. The broad surface of the plates showed three sets of striae and overlapping portions at angles of 56° to 63°, suggesting twinning. Cleavage at the edges was parallel to the striae and inclined at 76° to the cleavage parallel to the plates, again suggesting a possible monoclinic symmetry with the pseudo-hexagonal appearance arising from twinning. The chemical analysis by Mountain was in very close agreement with the formula CuMn_2O_4 .

DESCRIPTION

For the present investigation some plates of crednerite from the Mendip Hills were made available by the courtesy of the British Museum (Natural History) (BM 1923, 729). These correspond in physical properties, including form and cleavage, with the description of Spencer and Mountain. Two specimens from Friedrichroda labelled crednerite were examined but each was discovered to be incorrectly identified. The crystallographic study was therefore confined to the material from the Mendip Hills.

This crednerite consists of bright gray plates with a metallic lustre

which are striated on the broad surfaces in three directions. The angles between the striae in the plane of the plates were measured under a microscope as either about 55° or 69° . Cleaving along the perfect cleavage parallel to the plates produces flat highly reflecting surfaces which are unstriated. The plates are quite brittle, readily breaking parallel to the striations to produce very thin blade-shaped cleavage fragments.

A spectrographic analysis was made of an 0.2 mg. portion of the material. The powdered sample, mixed with 2 mg. of high purity carbon, was volatilized in the anode of a carbon arc on a Hilger Medium Quartz spectrograph. The spectrogram showed Cu and Mn as the two major elements, confirming the mineral as crednerite.

Under an ore-microscope the cleavage planes of crednerite are cream-white in color, with a reflectivity between 30% and 40%, estimated by visual comparison with minerals of known reflectivity. The prominent (001) cleavage is distinctly anisotropic in polarized light, and sometimes shows a mosaic intergrowth of two or three twin components each with a sharp but different extinction position. A slight tarnish was obtained with 20% HCl, while 30% HNO_3 , 20% KCN, 20% FeCl_3 , and saturated KOH and HgCl_2 had no effect after 1 minute. These properties observed in reflected light correspond to those given by Orcel and Pavlovitch (1932) for crednerite from Friedrichroda, except that the latter shows a non-persistent tarnish with 20% FeCl_3 .

CRYSTALLOGRAPHY

Sharp, clear rotation, and zero and first layer Weissenberg photographs were obtained with Cu radiation from a cleavage fragment of approximately square cross-section, for rotation about what was found to be the monoclinic b axis. Another set of single crystal photographs taken of a blade-shaped cleavage fragment show a pronounced diminution of the diffraction intensities in portions of the films. This is attributed to varying absorption of the x -ray beam within the fragment due to its much elongated cross-section, in the manner described by Wells (1937).

From the rotation photograph a lattice period of $2.877 \pm 0.005 \text{ \AA}$ was calculated for the axis of rotation. Both zero and first layer Weissenberg photographs show a plane point group symmetry of C_2 , for which the axis of rotation is either the [010] direction in a crystal of monoclinic symmetry, or the $[10\bar{1}0]$ direction in a crystal of rhombohedral diffraction symmetry $\bar{3} m$. The latter requires a rectangular cell in the zero and first layer, and in fact a small rectangular cell can be chosen on the reciprocal lattice sections plotted from the Weissenberg photographs. One period in this rectangular reciprocal plane lattice should then cor-

respond to the spacing of the $(10\bar{1}0)$ planes in the hexagonal lattice, perpendicular to the axis of rotation. The reciprocal lattice spacing of these planes was determined from the rotation photograph as 0.62 on a scale of λ/d ; the rectangular reciprocal lattice was however of dimensions 0.27×0.07 , so the rhombohedral possibility was discarded.

The smallest monoclinic cell with least obliquity was chosen, and its dimensions determined as

$$\begin{aligned} a &= 5.58 \pm 0.01 \text{ \AA} \\ b &= 2.87_7 \pm 0.005 \text{ \AA} \\ c &= 5.87_5 \pm 0.01 \text{ \AA} \\ \beta &= 104.0^\circ \pm 0.1^\circ \end{aligned}$$

The only systematic extinction conditions for this cell are in hkl diffractions, present only when $h+k$ is even. The cell is thus C centered, and the possible space groups are $C2/m$, $C2$ or Cm .

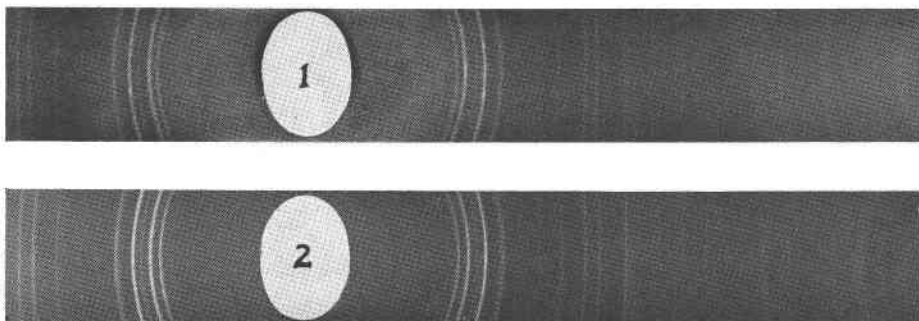


FIG. 1. X-ray powder patterns of 1: crednerite, Mendip, Hills
2: artificial $\text{Cu}_2\text{Mn}_2\text{O}_5$.

The x-ray powder pattern, Table 1, was indexed for this cell, and the agreement between observed and calculated spacings confirms both the diffraction lines of this pattern and the cell dimensions calculated from the single crystal photographs.

The lattice of crednerite also contains a monoclinic cell which has $\beta = 93^\circ$, and is thus geometrically pseudo-orthorhombic. This cell is of dimensions $a' = 7.05_5 \text{ \AA}$, $b' = 2.87_7 \text{ \AA}$, $c' = 9.03 \text{ \AA}$, $\beta' = 93.0^\circ$, and is twice the volume of the smaller C -centered cell. The orientation of the pseudo-orthorhombic cell is obtained from that of the unit cell selected by the transformation $10\bar{1}/010/\bar{1}0\bar{1}$.

CLEAVAGE

Twelve cleavage fragments were measured on a two-circle optical goniometer. In general the cleavage faces gave reflections of poor quality.

TABLE 1. CREDNERITE: X-RAY POWDER DATA
Fe radiation, Mn filter

Cu ₂ Mn ₂ O ₅ ¹ Synthetic		Crednerite Mendip Hills			
<i>I</i>	<i>d</i> (meas.) Å	<i>I</i>	<i>d</i> (meas.) Å	<i>hkl</i>	<i>d</i> (calc.) Å
6	2.85	6	2.85	(002)	2.85
9	2.67	10	2.71	{(200)	2.71
				{(201)	2.71
2	2.54	2	2.54	(110)	2.54
10	2.43	10	2.43	($\bar{1}$ 11)	2.43
2	2.25			{(202)	2.25
3	2.22	5	2.24 br.	{(201)	2.24
				{(111)	2.23
1	1.897	$\frac{1}{2}$	1.895	(003)	1.900
2	1.745	3	1.764	{(203)	1.769
				{(202)	1.762
3	1.615	4	1.613	($\bar{1}$ 13)	1.612
$\frac{1}{2}$	1.582	$\frac{1}{4}$	1.584		
3	1.552	4	1.560	($\bar{3}$ 11)	1.559
3	1.441	3	1.446	(020)	1.439
$\frac{1}{2}$	1.427		—		
$\frac{1}{2}$	1.414	2	1.409	{(204)	1.410
				{(311)	1.406
$\frac{1}{2}$	1.395		—		
$\frac{1}{4}$	1.348	$\frac{1}{2}$	1.359	{(402)	1.359
				{(400)	1.354
1	1.333	$\frac{1}{2}$	1.330	($\bar{3}$ 13)	1.332
1	1.287	$\frac{1}{2}$	1.287	(022)	1.284
2	1.269	1	1.273	{(221)	1.271
				{(220)	1.270
1	1.216	$\frac{1}{4}$	1.214	{(222)	1.213
				{(221)	1.211
$\frac{1}{4}$	1.173		—		
$\frac{1}{2}$	1.146br.		—		
1	1.128	$\frac{1}{4}$	1.129	{(402)	1.129
				{(404)	1.127
3	1.112	$\frac{1}{2}$	1.117	($\bar{2}$ 23)	1.116
1	1.091	1	1.091	{(313)	1.087
				{(115)	1.087
1	1.080	1	1.043	($\bar{5}$ 11)	1.039
$\frac{1}{2}$	1.068	$\frac{1}{2}$	1.009	{(224)	1.007
2	1.033			{(223)	1.005
1	1.024	1	0.989	{(422)	0.987
1	1.015			{(420)	0.986
3	1.011				
2	0.998				
$\frac{1}{2}$	0.993				
$\frac{1}{2}$	0.987				
$\frac{1}{2}$	0.980				

¹ Plus four weak lines 4.88— $\frac{1}{2}$, 3.02—1, 2.48—1, 2.03— $\frac{1}{2}$ from copper hausmannite.

The measurements reveal three prominent cleavage planes oblique to the cleavage in the plane of the plates. Two pairs of additional, poorer cleavage planes are also present in some fragments.

The angular positions of the cleavage planes are in accordance with the monoclinic symmetry of the single crystal x -ray photographs, but also show some pseudo-orthorhombic characteristics. From an instrumental correlation between the two-circle optical goniometer measurements and the diffractions recorded on the zero layer Weissenberg photograph, two of the prominent cleavages were identified as (001) parallel to the plane of the plates, and (100) oblique to this plane. By comparison with the crystallographic angles calculated from the unit cell dimensions, the

TABLE 2. CREDNERITE: MEASURED AND CALCULATED CLEAVAGE ANGLES*

Cleavage	Measured		No. of faces	Calculated	
	ϕ_2	ρ_2		ϕ_2	ρ_2
001:perfect	76°01'† (74°30'–78°10')	88°40'–90°	12	76°00'	90°00'
100:perfect	0°00'	88°30'–91°40'	12	0°00'	90°00'
$\bar{1}11$:good	121°–140°	32°–38°	5	129°54'	32°33'
111:poor	31°–38°	36°–42°	4	36°50'	39°14'
212:very poor	32°–37½°	45½°–47½°	2	36°50'	49°19'

* ϕ_2 and ρ_2 are given for the second setting of Palache, Berman, and Frondel (1944, p. 18) in the monoclinic system, in which the monoclinic b axis is vertical, with ρ_2 the angle from 010 and ϕ_2 measured positive clockwise from 100 in the direction of 001.

† Measurement from two cleavage fragments with sharp reflections from both (001) and (100).

other two prominent cleavage planes were identified as $\bar{1}11$; and in addition (111) as a poor cleavage, and (212) a doubtful cleavage observed as two reflections of very poor quality from only one fragment. The range of angles obtained from the better reflections, together with the angles calculated from the cell dimensions, are listed in Table 2.

TWINNING

The intergrowth seen in reflected polarized light is undoubtedly due to twinning. On one fragment, each of the three components A , B , C , corresponds to one of the three directions of striae present on the 001 crystal face. On any one part of this surface striae are present in one direction only, and the border marking change of direction of the striae corresponds exactly with the boundaries of the intergrowth observed in reflected polarized light.

The nature of the twinning was determined by measuring the cleavage of this fragment with a two-circle goniometer, distinguishing the cleavage planes on each of the three components. On a stereographic projection, Fig. 2, it is seen that the adjacent components *A* and *B* are in a definite crystallographic relationship; for within the accuracy of the measurements the $4\bar{1}\bar{1}$ planes of each component are parallel, and on rotation of *A* an angle of 180° around the normal to its $4\bar{1}\bar{1}$ plane the exact orientation of the component *B* is obtained. The adjacent components *B* and *C* of the fragment are in similar twin relationship, the $4\bar{1}\bar{1}$ planes of each

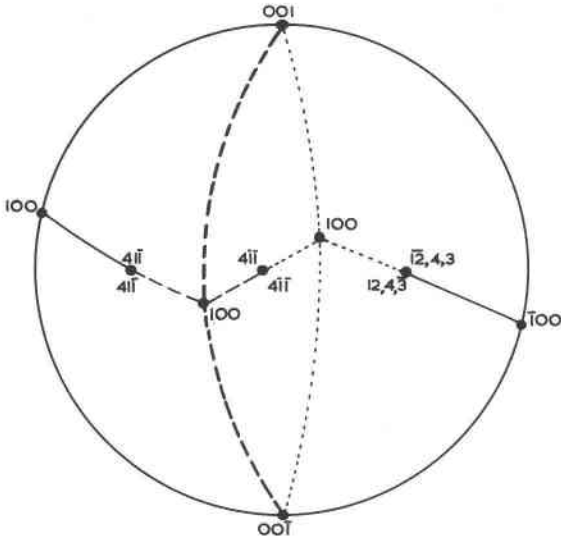


FIG. 2. Stereographic projection of twinned crystal of crednerite. (001) is common to the three components, distinguished by the solid and coarse and fine dashed lines. The indices of faces which are parallel in the two components are given on the appropriate side for each component.

being parallel, and the orientation of one related to that of the other by a 180° rotation around the normal to this plane. The components *C* and *A* of the twin, although actually related in orientation through the component *B*, form a pseudotwin, in which the orientation of one may be derived from that of the other by a 180° rotation about a line inclined at $2\frac{1}{2}^\circ$ to the normal to the $\bar{1}2, 4, 3$ plane.

The twinning conforms to the normal type of rotation twin in which the twin axis is normal to a possible face of the crystal. In some of the crednerite plates 001 appears to be a composition plane, and in one fragment the (100) cleavage is stepped parallel to the 001 plane, supporting

this observation. Nevertheless, in reflected light the twinned components are seen to be complexly intergrown on some (001) surfaces.

The prominent 001 face, parallel to the broad surface of the crednerite plates, is almost parallel in both components of a crystal twinned on this (41 $\bar{1}$) law. However the intersection of (100) with (001), which is the direction [010] of the striae on the broad faces of the plates, is rotated an angle of 56° in one twin component relative to the other. In a crystal twinned twice on this law, the three directions of striae on the parallel (001) faces are at angles of 56°, 56° and 68°, producing the pseudo-hexagonal appearance which was noted by Spencer and Mountain.

TWINNING FROM X-RAY SINGLE CRYSTAL PHOTOGRAPHS

An intergrowth with the relative orientation of the pseudotwin was also found on one set of the single crystal *x*-ray photographs. One rotation photograph about the *b* axis of a blade-shaped cleavage fragment has ten closely spaced layer lines, of which the zero and sixth are far stronger than the others, and coincide with the zero and first layers normally obtained on rotation about this axis of period 2.87 Å. In addition, the central part of some of the layer lines have no diffraction spots, and this gap varies systematically from a maximum for the third and eighth layers to nil for the zero, fifth and sixth layers. The gap in the third layer line extends for two-thirds the width of the rotation photograph, which records the complete cone of diffractions of each layer except for a small gap of 1/15 of the circumference of each cone at intersection with the film. The spacing of the layers corresponds to a real lattice period of 17.3 Å along the axis of rotation.

A Weissenberg resolution of the zero layer gave the normal *h*0*l* reciprocal plane lattice of crednerite. However, the weak first layer gave diffractions on a Weissenberg photograph corresponding to only a single line in the reciprocal lattice, with a repetition unit equal to *c**. This line parallel to *c**, which constitutes the first layer line, is a distance determined as 0.60 from the central 000 point of the reciprocal lattice at a scale of λ/d , and at a height 0.089 above the zero level. A cross-section of the reciprocal lattice of crednerite perpendicular to the *c** axis, Fig. 3, shows that the four lines 1 and 5 are the only reciprocal lattice lines parallel to *c** which are a distance 0.60 from the origin and contain points corresponding to possible *hkl* diffractions. A small portion of the crednerite cleavage fragment used for this set of single crystal photographs was therefore in an orientation such that one of these four lines, which are crystallographically equivalent, was parallel to the plane of the zero-level diffractions and a distance 0.089 from this plane. The zero-level must therefore be one of the planes perpendicular to the cross-section,

Fig. 3, and intersecting it along AA' , BB' , or the equivalent directions A_1A_1' , B_1B_1' .

Consider the rotation photograph of crednerite oriented with the axis of rotation perpendicular to $AA'c^*$. Reciprocal lattice points lie along lines 0, 1, 2, 3, & 3', 4, \dots , parallel to the zero layer and at equal increments of 0.089 from it. The corresponding diffractions fall along layer lines spaced according to a real lattice period of 17.3 Å; and each layer (except one) arises from one reciprocal lattice line. The reciprocal lattice

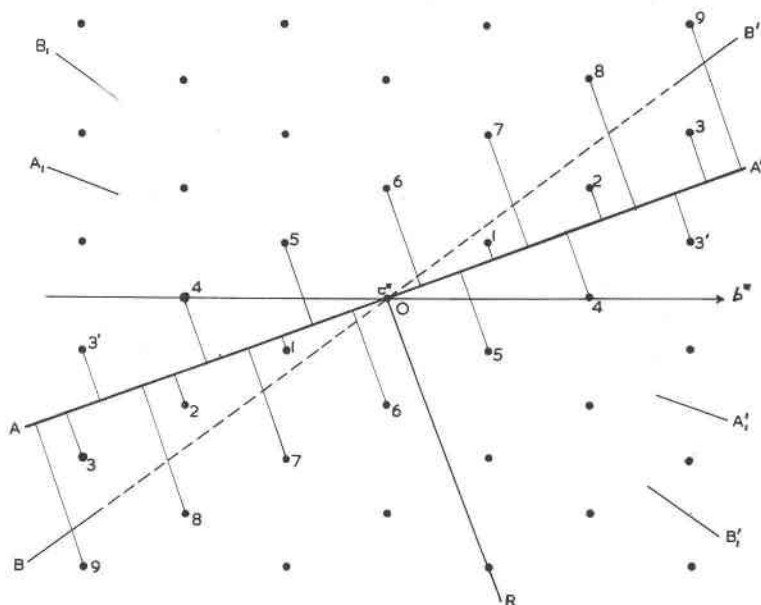


FIG. 3. Section through the centre of the reciprocal lattice of crednerite perpendicular to c^* . Dots mark the position of lines parallel to c^* in the reciprocal lattice which contain the points, with $h+k=2n$, for which diffractions may occur.

lines corresponding to the third and ninth layers are distant from the axis of rotation, and, with all points having high values of ξ^1 , diffractions appear only at each extremity of the layer line. The other lines are at smaller distances from the axis of rotation, and have smaller central gaps in the corresponding layer line on the rotation photograph. These gaps exactly correspond to, and account for, those observed in the rotation photograph and described above.

The measurements on the rotation and Weissenberg photographs also allow the plane $BB'c^*$ as zero-layer at a distance 0.089 from line 1 in the

¹ ξ : The distance, in the reciprocal lattice, from the axis of rotation.

reciprocal lattice. However, the distances from this plane to the reciprocal lattice lines parallel to c^* do not correspond to the layer-line spacings, so this orientation is rejected.

The interpretation of these single crystal photographs determines the relative orientation of the two components giving the strong and weak layers respectively. The intergrowth is such that the 001 planes of each component are parallel, and the directions [010] of the major component, and [320] of the minor component, normal to $AA'c^*$, are parallel to the axis of rotation. The orientation of one component is obtained from that of the other by rotation of 180° about a line inclined from the normal to the $\bar{1}2, 4, 3$ plane, towards b at $2\frac{1}{2}^\circ$; the relationship found by optical goniometer measurements between two components each actually twinned with a third component by 180° rotation about the normal to $4\bar{1}\bar{1}$.

The interpretation of the rotation photograph also provides examples of a layer-line composed of diffractions corresponding to only a single line in the reciprocal lattice. These diffractions form prominent layer-lines when the axis of rotation is slightly inclined to a direction of small repetition distance in the crystal lattice, and is also perpendicular to a line of small repetition distance in the reciprocal lattice—thus being parallel to a crystallographic plane with low hkl indices. In the example described the axis of rotation, OR in Fig. 3, lies in the 001 plane and is inclined at 8° to [110]. Rotation about an axis in 001 at any lower inclination to [110] would likewise give layer lines, corresponding to the reciprocal lattice lines parallel to [001], although there is no lattice row in the crystal along the axis of rotation. Such rotation photographs would show, relative to that for 8° inclination, a splitting of the third layer line into two layer lines, and have layer lines in two groups, three more closely spaced on each side of the zero layer, and three more closely spaced on each side of the former sixth layer. The layer lines within these two groups become progressively closer with decreasing inclination, and coincide to form the zero and first layers respectively for rotation about [110], at zero inclination.

The occurrence of such layer lines, *without* a zone axis and lattice row of the crystal parallel to the axis of rotation would generally be revealed by a non-regularity in spacing of the outer layer lines relative to the inner, or by the absence of spots in the front diffraction portion of some layer lines. The spacing of such layer lines is not a measure of a lattice period along the axis of rotation. In addition, the normal explanation of layer lines as diffractions restricted to cones around the axis of rotation, the angle of the cones determined by the lattice period along this axis and the x -ray wavelength, does not apply.

UNIT CELL CONTENTS

Crednerite from the Mendip Hills has been analyzed by Mountain (Spencer and Mountain, 1923). Although the analysis, as corrected for 1.05% cerussite and 6.10% malachite, gives a Cu:Mn:O ratio close to 1:2:4, the calculated cell contents, Table 3, are quite irrational. The

TABLE 3. CREDNERITE—ANALYSIS AND UNIT CELL CONTENTS

	1	2		3
MnO	54.40	58.62	Mn	2.29
CuO	36.57	34.68	Cu	1.16
O	6.22	6.70	O	4.66
H ₂ O	1.88	—		
CO ₂				
PbO	0.88	—		
Total	99.95	100.00	D(meas.)	5.03

1. Crednerite, Mendip Hills, analysis of Mountain (Spencer and Mountain, 1923).

2. The same, after deducing 1.05% cerussite, 6.10% malachite, and recalculation to 100%.

3. Atomic contents of the unit cell, calculated for density of 5.03.

closest rational cell contents of CuMn_2O_4 requires a density of 4.32 gm./cc., which is far below the value 5.03 obtained by Mountain for crednerite from the Mendip Hills, and the densities of 4.96 to 5.03 given by Credner (1847, 1848) and by Rammelsberg (1849) for crednerite from Friedrichroda.

SYNTHESIS

The seven analyses of crednerite from Friedrichroda published by Credner (1847, 1848) and by Rammelsberg (1849) show wide variation. Omitting a small BaO content, two of the analyses correspond closely to the composition $\text{CuO} \cdot \text{Mn}_2\text{O}_3$ of crednerite from the Mendip Hills. Analyses of higher copper content correspond to compositions close to $3\text{CuO} \cdot 2\text{Mn}_2\text{O}_3$ and to $4\text{CuO} \cdot 3\text{Mn}_2\text{O}_3$, and one analysis corresponds to a composition of $2\text{CuO} \cdot 3\text{Mn}_2\text{O}_3$. Because of this variation of analyses, and the irrational unit cell contents obtained from the crystallographic study, synthetic crednerite was prepared and analyzed.

Intimate mixtures of copper and manganese oxides were prepared by adding a solution of the sulfates to an excess of NaOH solution, which gave complete precipitation of the copper and manganese. After washing with hot distilled water, the precipitates were air dried at 150° C., finely ground, and then shaken with four steel balls in 1 oz. bottles for five minutes to ensure complete mixing. The resulting powders were briquetted into small tablets in a hydraulic press.

Tablets with Cu:Mn=1:2 were heated on platinum foil at temperatures of 1100° to 1300° C. for 1 to 24 hours, and then quenched in air. In polished section these tablets are completely crystalline, consisting of intergrowths of copper hausmannite and crednerite. The hausmannite phase predominates, varying in proportion from about 65% to over 90%, and increases with the time and temperature of heating. Occasional crystals of cuprite occur within the crednerite in the hausmannite-rich tablets. The hausmannite phase probably approaches CuMn_2O_4 in composition, and has an x-ray powder pattern similar to MnMn_2O_4 , differing slightly in the spacing of the lines which correspond in position to a tetragonal cell of dimensions $a=5.75$, $c=9.36$ Å.

The products of heating for 3 hours at 1135° C. a series of tablets with

TABLE 4. SYNTHETIC CREDNERITE—COMPOSITION AND CELL CONTENTS

	1	2	3	4	5	6	
CuO	64.71	52.1	48.57	51.2	50.2	Cu	1.73
MnO	33.56	42.7	46.50	44.2	44.8	Mn	1.73
O	1.73	5.2	4.93	4.6	5.0	O	4.33
Total	100.00	100.0	100.00	100.0	100.0	Density	5.00

1. Analysis by G. C. Carlos.
2. The same, after deducing 21.3% Cu_2O and recalculation to 100%.
3. Analysis by G. C. Carlos.
4. The same, after deducing 15% CuMn_2O_4 and recalculation to 100%.
5. $\text{Cu}_2\text{Mn}_2\text{O}_5$.
6. Unit cell contents for composition $\text{Cu}_2\text{Mn}_2\text{O}_5$.

Cu:Mn atomic ratios greater than 1:2 include two in which crednerite predominates. One of these consists in polished section of tabular crystals of crednerite up to 0.3 mm. across, with interstitial cuprite. Micrometric analysis determined the amount of cuprite as 18% by volume. The other contains tabular crystals of crednerite about 0.03 mm. across, together with 15% by volume of the hausmannite phase. The chemical analyses of portion of these tablets are given in Table 4, (1) and (3), together with the composition of the crednerite, obtained by deducing 21.3% by weight of cuprite, (2), and 15% by weight of CuMn_2O_4 , (4). In each analysis the oxygen content is taken as the difference of $\text{CuO} + \text{MnO}$ from 100.00.

The analyses show that the composition of the synthetic crednerite is close to $\text{Cu}_2\text{Mn}_2\text{O}_5$, in contrast to the composition CuMn_2O_4 given by the analysis of the Mendip Hills material. The analyses of Friedrichroda crednerite with the highest copper content are however more comparable with the synthetic product.

The x-ray powder pattern of synthetic crednerite is similar to that of the Mendip Hills crednerite, Table 1. The small differences in spacing of some lines indicate the a dimension of the former is 1% smaller. The unit cell content of crednerite of composition $\text{Cu}_2\text{Mn}_2\text{O}_5$, calculated for a cell volume 1% smaller than that of the natural material, and the measured density of 5.00 gm./cc. is given in Table 4.

The cell contents are again quite irrational, and in oxygen content lower than the Mendip Hills crystals. For the composition $\text{Cu}_2\text{Mn}_2\text{O}_5$ the smallest multiple of the monoclinic cell which contains a nearly rational number of atoms is one of thrice the volume. However, there is no evidence in the x-ray single crystal photographs for tripling of any of the unit cell dimensions.

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REFERENCES

- CREDNER, H. (1847), Über das Vorkommen von Vanadinsurem Kupfer-Oxyd und Kupfer-Manganerz bei Friedrichroda im Thüringer Wald: *Neues Jahr.*, **1847A**, 1.
- CREDNER, H. (1848), Über das Vorkommen des Vanadinsuren Kupfers und des Mangankupfers bei Friedrichroda am Thüringer Wald: *Annalen der Physik*, **74**, 546.
- ORCEL, J., AND PAVLOVITCH, ST. (1931), Les caracteres microscopique des oxydes de manganese et des manganites naturels: *Bull. Soc. Mineral. Franc.*, **54**, 108.
- PALACHE, C., BERMAN, H., AND FRONDEL, C. (1944), Dana's System of Mineralogy, 7th Edition, Vol. 1. John Wiley, New York.
- RAMMELSBURG, C. (1849), Über den Crednerit, ein Mangan-Kupfererz von Friedrichroda am Thüringer: *Annalen der Physik*, **75**, 559.
- SPENCER, L. J., AND MOUNTAIN, E. D. (1923), New lead-copper minerals from the Mendip Hills (Somerset): *Mineral. Mag.*, **20**, 69.
- WELLS, A. F. (1937), A note on absorption and Weissenberg photographs: *Zeits. Krist.*, **96**, 451.

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