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The Crystal Structure of Chalcophanite, $ZnMn_3O_7 . 3H_2O$

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Chalcophanite, $ZnMn_3O_7 . 3H_2O$, crystallizes in the triclinic system with $a = 7{\cdot}54$, $b = 7{\cdot}54$, $c = 8{\cdot}22$ Å, $\alpha = 90°$, $\beta = 117{\cdot}2°$, $\gamma = 120°$, space group $P\bar{1}$. The structure determination, based upon Fourier projections, was aided by first considering that of a prominent sub-cell with monoclinic symmetry, space group $C2/m$, with $a_m = 4{\cdot}95$, $b_m = 2{\cdot}85$, $c_m = 7{\cdot}17$ Å, $\beta_m = 103°\ 30'$, related to the real cell by the index transformation monoclinic → triclinic $= \frac{5}{7}, \frac{1}{7}, 0/\frac{1}{7}, \frac{3}{7}, 0/\frac{3}{7}, \frac{2}{7}, 1$. The structure consists of single sheets of water molecules grouped in open double hexagon rings alternating with double oxygen layers in which six of every seven octahedral sites are occupied by manganese. Zinc atoms linked to the triads of oxygens bounding the vacancies in the manganese layer complete their octahedral coordination with triads of water molecules. A scheme of additional bonding between sheets, based upon hydrogen bridges between water and oxygen, is described. The electron-density projections afford direct evidence of fractional amounts of interstitial zinc ions, leading to better agreement between the X-ray evidence and the chemical and density data.

Introduction

The structure of chalcophanite was determined as part of an examination of the crystal chemistry of the manganese oxide minerals with defect structures. Although it is found in several local Australian ores, the specimen of chalcophanite most suited to detailed X-ray examination came from the Sterling Hill region, New Jersey, U.S.A., whence it was first reported by Moore (1875). The crystals upon which the present description is based were from specimen C1814 of the Canfield collection, Smithsonian Institution, U.S. National Museum, by courtesy of Dr George Switzer, who stated it to be from the same locality as Moore's material. It proved subsequently to be identical with a further specimen sent by Dr C. Frondel from the Harvard collection.

Some precautions to ensure the identity of chalcophanite are necessary since at least four hydrous oxides with Zn and Mn as the principal constituents (Frondel, 1953), differing little in empirical formula and possibly non-stoichiometric in composition, are known.

Chalcophanite crystals in the form of thin lamellae encrust a massive matrix in the Sterling Hill specimens. They possess a characteristic purplish-black colour, are readily cleaved parallel to (001) and occasionally are developed as minute and somewhat irregular octahedra too small for convenient manipulation. The chemical formula quoted in *Dana's System of Mineralogy* (1944) as $(Zn, Mn)Mn_2O_5 . 2H_2O$ was based upon the belief that Mn^{2+} and other divalent ions substitute for Zn. This X-ray analysis shows that the formula $ZnMn_3O_7 . 3H_2O$, recorded previously for a specimen of chalcophanite with no divalent manganese, found locally at Buchan, Victoria (Wadsley, 1950), is an ideal, and the evidence supports a variable formula based upon certain structural characteristics.

Determination of the unit cell

The crystal was readily set upon what appeared to be a symmetry axis of 2·85 Å, but well exposed oscillation photographs exhibited weak asymmetrical subsidiary layer lines. Thus on a rotation photograph only the seventh, fourteenth etc. layer lines, corresponding to the pseudosymmetry, were at all pronounced.

Because of this evidence for a large unit cell, a series of equi-inclination Weissenberg exposures for the first eight levels were taken, using filtered copper radiation. The sub-cell, determined by the zero and seventh levels, was monoclinic with

$$a_m = 4{\cdot}95,\ b_m = 2{\cdot}85,\ c_m = 7{\cdot}17 \text{ Å},\ \beta_m = 103°\ 30'$$

and centred on (001), giving the choice of space groups Cm, $C2$, or $C2/m$. To facilitate the choice of axes for the real cell, each of the eight levels was plotted on to a sheet of perspex, the eight sheets placed one on top of the other in the correct manner then representing clearly the three-dimensional reciprocal lattice.

Let a_m^*, b_m^*, c_m^* and β_m^* be the sub-cell reciprocal elements. The origins of each of the weakly diffracting levels were seen to fall on a line from the origin to the point 513. Thus the seventh level, corresponding to the first level of the sub-cell, is displaced by $5a_m^*$, b_m^* and $3c_m^*$, and each subsidiary level by $n/7$ths of these values. It is now possible to determine the axial lengths of any other unit cell in terms of the values measured for the sub-cell. With an arbitrary system of indexing, and a point hkl chosen as a new axial element, the length of the reciprocal axis is readily found by triangulation which gives in this instance a function of the form

$$t^* = \sqrt{\{[a_m^*(\tfrac{5}{7}k+h)]^2+[c_m^*(\tfrac{3}{7}k+l)]^2 - 2a_m^*c_m^*(\tfrac{5}{7}k+h)(\tfrac{3}{7}k+l)\cos(180-\beta_m^*)+(k\zeta)^2\}}\,,$$

where ζ is the subsidiary layer-line spacing.

The unit cell eventually selected was triclinic and related to the sub-cell by the index matrices (*International Tables*, 1952):

monoclinic → triclinic = $\frac{5}{7}, \frac{1}{7}, 0/\frac{1}{7}, \frac{3}{7}, 0/\frac{3}{7}, \frac{2}{7}, 1$;
triclinic → monoclinic = $\frac{3}{2}, -\frac{1}{2}, 0/-\frac{1}{2}, \frac{5}{2}, 0/-\frac{1}{2}, -\frac{1}{2}, 1$.

The lengths of the new inverse cell constants were computed, and are listed in Table 1 with their direct components. These values were subsequently confirmed by measurements on the triclinic unit cell.

Table 1. *Triclinic elements of chalcophanite*

(Cu $K\alpha$ radiation)

a^* =	0·279	a =	7·54 Å
b^* =	0·248	b =	7·54 Å
c^* =	0·221	c =	8·22 Å
α^* =	72·6°	α =	90°
β^* =	58·1°	β =	117·2°
γ^* =	55·8°	γ =	120°
		Volume =	343·5 Å^3

The manner in which the two unit cells are related in direct space is shown in Fig. 1.

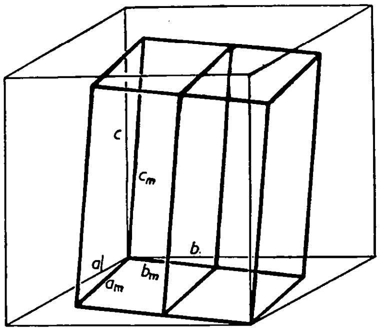


Fig. 1. Relation between the sub-cell (thick lines) and the real cell (thin lines). Only the sub-cells are drawn in clinographic projection.

The pseudosymmetry of chalcophanite

The identity of the a and b axes, inclined at 120° to each other, and the value of 90° found for α, suggested strongly that the triclinic elements might be replaced by others of higher symmetry.

In his description of this mineral, Moore (1875) claimed that the symmetry was rhombohedral. The triclinic zone axes [111], [101] and [001] are in fact equal in length (8·22 Å) and, moreover, are mutually inclined at an angle $\alpha' = 54{\cdot}6°$. From the crystal geometry, it is evident that, if it existed, the trigonal axis would be normal to the prominent basal cleavage. A Laue photograph of a crystal mounted in this way showed no symmetry, however, and Moore's doubtful rhombohedral setting is therefore incorrect.

A further possible choice of monoclinic axes related by the expression

$$\text{monoclinic} \rightarrow \text{triclinic} = 1\bar{1}0/110/001$$

failed to give the necessary diffraction evidence, and no further attempt was made to provide proof of symmetry higher than $P\bar{1}$.

Structure determination

The structure of the sub-cell was first determined by projection along the b_m axis, i.e. the [130] zone axis of the triclinic unit cell. That of the real cell was then found from the b-axis projection. Although inclined at only 19° to each other, these provided all the data necessary to determine the atomic parameters.

Intensities were recorded for these two axes by the multiple-film technique, the films being separated one from the other by tinfoil to increase the inter-film factor. Measurements of intensity were made by comparing the spots for each film in the multiple exposure with a set of spots of known intensity ratio prepared by exposing a single reflexion with a 5° Weissenberg motion for varying time intervals. The measurements corrected for Lorentz and polarization factors by the usual methods, and weighted with a temperature factor $B = -0{\cdot}8$ Å^2, were subsequently placed on an absolute scale by comparing with the structure factors calculated for the final model.

A test for piezoelectricity proved negative, and the structure was assumed to be centrosymmetric.

The density, the mean of six measurements on a torsion microbalance, was $3{\cdot}98 \pm 0{\cdot}02$ g.cm.$^{-3}$. The chemical composition was assumed to be that given by Moore (1875) for crystals of chalcophanite from Sterling Hill. The formula, $ZnMn_3O_7.3H_2O$, gave a density of 3·83 g.cm.$^{-3}$ calculated for $Z = 2$, considerably lower than the measured value. A value of 4·01 g.cm.$^{-3}$ was found for $Zn_2Mn_7O_{14}.5H_2O$. Both formulae could be made to agree roughly with the chemical analysis, assuming that different types of ionic replacement or of partly filled sites could occur in the structure. It was decided, therefore, that the ideal chemical formula of this mineral should be determined by the structure analysis.

The structure of the sub-cell

Since the volume of the sub-cell is two-sevenths that of the real cell, the contents do not involve rational numbers of atoms. It was obvious that only the O atoms could be placed with any certainty, and these were located in the fourfold positions listed in the *International Tables* for the centrosymmetric space group $C2/m$. It was assumed that the Mn atoms were in a twofold site which could arbitrarily be chosen as the origin, and these, the principal scattering components, could well dominate the phases of all the reflexions. A Fourier projection of the structure along the b_m axis was computed, all the observed F's being given a positive sign. Depicted in Fig. 2, this showed four distinct scattering elements which evidently corresponded to Mn, O, Zn and H_2O.

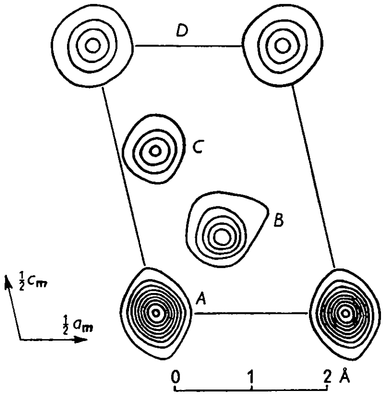


Fig. 2. Fourier projection of the sub-cell structure along the b_m axis.

The interpretation of the structure from this projection raised some difficulties. It was evident from the nature of the mineral that it had a layer structure, yet the most obvious explanation based upon the close packing of oxygen and water or hydroxyl layers was found to be untenable. Assuming the metal atoms to be in octahedral coordination and the structure to have a centre of symmetry, all atoms lie in special positions on the b_m axis. Atom A, selected as Mn, is distant 1·94 and 1·96 Å from atoms B. These values are the normal Mn^{4+}–O distances, and hence B is evidently oxygen. The distances B–C are 1·93 and 1·98 Å, so that C cannot be H_2O or OH. Hence the peak C must be Zn, which is further linked to D with bonds of length 2·15 Å. These latter are evidently water molecules.

Structure factors for this projection were calculated only when details of the triclinic cell were available. This projection was then refined by an $F_o - F_c$ synthesis, giving the parameters and the interatomic distances for the sub-cell in Tables 2 and 3.

Table 2. *Atomic parameters of the monoclinic sub-cell*

Space group $C2/m$ (0, 0, 0; ½, ½, 0)+

	x	y	z
$\frac{12}{7}$ Mn in 2(a)	0	0	0
4 O in 4(i)	−0·280	0	0·150
$\frac{4}{7}$ Zn in 4(i)	0·099	0	0·304
$\frac{12}{7}$ H_2O in 2(d)	0	½	½

Table 3. *Interatomic distances for the sub-cell*

Zn–O	1·93 Å	H_2O–H_2O	2·85 Å
Zn–O	1·98	Mn–O	1·96
Zn–H_2O	2·14	Mn–O	1·94
Zn–H_2O	2·15	O–O	2·85
H_2O–O	2·94	O–O	2·65
H_2O–O	2·96	O–O	2·68

The structure of the triclinic cell

Because of the disparity in the observed and theoretical densities, it was uncertain at this stage whether six or seven manganese atoms were present in the unit cell. However, for either case the parameters, together with those of the oxygens, could be deduced from the geometrical relationship of the sub-cell to the real one. If seven Mn were present, one would be at the origin, the remaining six in twofold positions in the plane at $z = 0$. If six, the atom at the origin would be absent. The Mn and O atoms in both cases would contribute principally to the (00l) and (70l) reflexions of {h0l}.

There were four positions that the zinc atom could occupy in the plane at $z = 0·30$, and it was reasoned that the most rapid method for deciding between them was by means of a difference Patterson projection $P(u, w)$ computed by omitting the (00l) and (70l) terms. This gave a single prominent peak (Fig. 3(a))

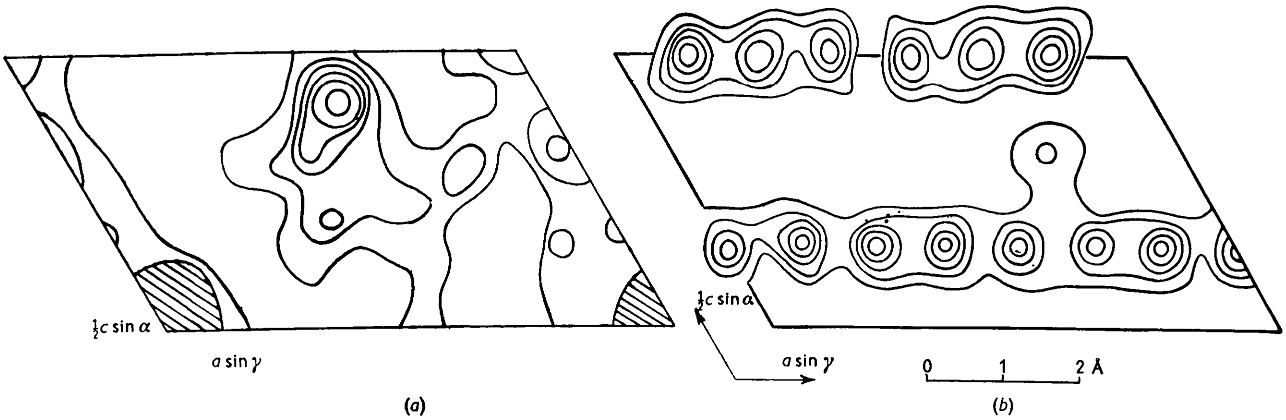


Fig. 3. (a) Difference Patterson projection $P(u, w)$ of the triclinic structure. The (00l) and (70l) terms were omitted so that the Zn–Zn vector would be enhanced.

(b) Difference Fourier projection along the b axis, showing oxygen, water, and the minor peak.

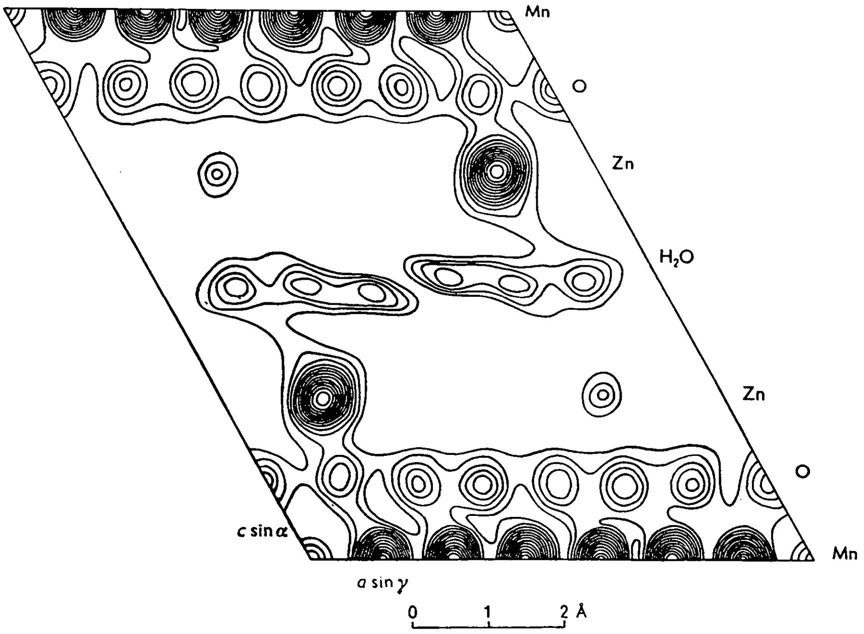


Fig. 4. Fourier projection of the structure along the b axis.

evidently due to the Zn–Zn vector across the centre of symmetry and providing the parameters $x = 0{\cdot}20$, $z = 0{\cdot}30$ for the Zn atom. The z value was in close agreement with that obtained for it in the sub-cell. Structure factors were computed for the whole zone of reflexions $\{h0l\}$. The zinc atom was given the parameters above, the oxygens at $z = 0{\cdot}15$ and with values of x from $0, a/7, 2a/7, \ldots,$ to $6a/7$. The best fit with the observed F's was found by omitting the Mn atom at the origin, with the remaining Mn atoms in the twofold positions at $z = 0$, and with x having the values $a/7$, $2a/7$ and $3a/7$.

In order to refine these values, and to locate the water molecules, a Fourier projection along the b axis was made, the signs being determined by these structure factors. This is shown in Fig. 4. The metals and oxygens were clearly resolved, and the water molecules at $z = \frac{1}{2}$ appeared as three somewhat distorted peaks at $a/7$, $2a/7$ and $3a/7$ approximately. Further refinement of the Zn parameters led to a new set of structure factors, this time including the contributions of the water molecules but without changing any signs. This reduced the discrepancy between F_o and F_c to 17%. Finally an $F_o - F_c$ synthesis was made by subtracting the computed Mn and Zn contributions from the observed structure amplitudes. Illustrated in Fig. 3(b), this showed considerable improvement in the shape of the water peaks and a refinement of the oxygen parameters. A small peak at the origin of the F_o synthesis (Fig. 4) was removed, but there remained a small scattering component of height approximately 3 e.Å^{-2} at $x = 0{\cdot}75$, $z = 0{\cdot}30$ (Figs. 3(b) and 4). The significance of this is discussed below.

Table 4. *Atomic parameters of chalcophanite*

All atoms in the general positions 2(i) for the space group $P\bar{1}$

	x	y	z
Mn_1	$\frac{1}{7}$	$\frac{3}{7}$	0
Mn_2	$\frac{2}{7}$	$\frac{6}{7}$	0
Mn_3	$\frac{3}{7}$	$\frac{2}{7}$	0
Zn	0·202	0·099	0·304
O_1	0	$\frac{3}{7}$	0·150
O_2	$\frac{1}{7}$	$\frac{6}{7}$	0·150
O_3	$\frac{2}{7}$	$\frac{2}{7}$	0·150
O_4	$\frac{3}{7}$	$\frac{5}{7}$	0·150
O_5	$\frac{4}{7}$	$\frac{1}{7}$	0·150
O_6	$\frac{5}{7}$	$\frac{4}{7}$	0·150
O_7	$\frac{6}{7}$	0	0·150
$(H_2O)_1$	$\frac{1}{7}$	$\frac{13}{14}$	$\frac{1}{2}$
$(H_2O)_2$	$\frac{2}{7}$	$\frac{5}{14}$	$\frac{1}{2}$
$(H_2O)_3$	$\frac{3}{7}$	$\frac{11}{14}$	$\frac{1}{2}$

The final parameters of the triclinic unit cell (Table 4) were obtained by geometry from the two projections. A list of F_o and F_c are given in Table 5, the overall discrepancy being 15%. A complete list of interatomic distances was not evaluated. Deviations in the x parameters of the oxygens and waters from the n/7ths required by the sub-cell relationship were of the order ±0·005 and were not considered significant. The sub-cell interatomic distances in Table 3 may therefore be taken as representative of the structure as a whole.

Description of the structure

From the X-ray evidence, it is clear that chalcophanite has the ideal formula $ZnMn_3O_7.3H_2O$. It has a layer structure (Figs. 4 and 6) with the sequence

$$-Mn-O-Zn-H_2O-Zn-O-Mn-;$$

Table 5. *Observed and calculated F's for chalcophanite (triclinic indices)*

(Filtered molybdenum radiation)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	61	67	204	17	$\overline{19}$	$\bar{3}14$	62	58
002	40	47				$\bar{3}15$	95	85
003	17	17	$\bar{7}05$	26	27	$\bar{3}16$	17	17
004	33	40	$\bar{6}05$	<10	$\bar{6}$	$\bar{3}17$	12	16
005	12	12	$\bar{5}05$	17	$\overline{18}$	$\bar{3}18$	16	21
006	47	49	$\bar{4}05$	14	$\overline{12}$	$\bar{3}19$	25	25
007	36	45	$\bar{3}05$	8	10	$\bar{3},1,10$	13	13
008	27	35	$\bar{2}05$	21	10	$\bar{3},1,11$	30	41
009	<12	9	$\bar{1}05$	$\bar{9}$	$\bar{7}$	$\bar{3},1,12$	23	19
0,0,10	17	23	500	13	7			
						$6\bar{2}8$	14	8
$\bar{7}01$	33	31	$\bar{7}06$	24	30	$6\bar{2}7$	16	17
$\bar{6}01$	<10	5	$\bar{6}06$	16	$\overline{16}$	$6\bar{2}6$	17	25
$\bar{5}01$	10	$\bar{9}$	$\bar{5}06$	<9	$\bar{5}$	$6\bar{2}5$	11	11
$\bar{4}01$	23	$\overline{21}$	$\bar{4}06$	<9	7	$6\bar{2}4$	18	22
$\bar{3}01$	10	$\overline{12}$	$\bar{3}06$	<8	1	$6\bar{2}3$	15	18
$\bar{2}01$	12	13	$\bar{2}06$	23	$\overline{17}$	$6\bar{2}2$	9	11
$\bar{1}01$	12	17	$\bar{1}06$	15	$\overline{20}$	$6\bar{2}1$	15	14
100	7	$\bar{6}$	600	<11	$\bar{1}$	$6\bar{2}0$	64	55
101	31	$\overline{30}$	106	<10	5	$\bar{6}21$	34	33
201	11	$\overline{13}$	206	<11	0	$\bar{6}22$	46	37
301	9	8	306	12	$\bar{9}$	$\bar{6}23$	40	37
401	<9	7				$\bar{6}24$	27	31
501	<10	$\bar{6}$	$\bar{7}07$	26	25	$\bar{6}25$	<5	6
601	14	$\overline{13}$	$\bar{6}07$	<10	3	$\bar{6}26$	42	38
701	19	17	$\bar{5}07$	10	7	$\bar{6}27$	40	38
			$\bar{4}07$	<9	$\bar{5}$	$\bar{6}28$	30	32
$\bar{7}02$	27	29	$\bar{3}07$	16	$\overline{17}$	$\bar{6}29$	23	24
$\bar{6}02$	19	$\overline{15}$	$\bar{2}07$	<9	$\overline{12}$	$\bar{6},2,10$	23	32
$\bar{5}02$	19	$\overline{19}$	$\bar{1}07$	<9	3	$\bar{6},2,11$	<9	4
$\bar{4}02$	<7	$\bar{4}$	700	26	26	$\bar{6},2,12$	<10	9
$\bar{3}02$	14	9	107	<10	$\bar{3}$	$\bar{6},2,13$	13	15
$\bar{2}02$	9	$\bar{3}$	207	12	$\overline{11}$	$\bar{6},2,14$	18	16
$\bar{1}02$	33	$\overline{32}$						
200	38	$\overline{30}$	$\bar{7}08$	39	42	$9\bar{3}3$	12	14
102	<6	$\bar{8}$	$\bar{6}08$	<11	1	$9\bar{3}2$	24	22
202	10	9	$\bar{5}08$	<10	12	$9\bar{3}1$	27	25
302	<8	$\bar{1}$	$\bar{4}08$	13	$\overline{13}$	$9\bar{3}0$	11	7
402	18	$\overline{15}$	$\bar{3}08$	<10	$\bar{5}$	$\bar{9}31$	15	18
502	10	$\overline{14}$	$\bar{2}08$	<10	$\bar{5}$	$\bar{9}32$	15	13
602	<12	$\bar{3}$	$\bar{1}08$	<10	1	$\bar{9}33$	13	14
702	22	25				$\bar{9}34$	22	19
			$\bar{7}09$	15	16	$\bar{9}35$	45	43
$\bar{7}03$	<11	1	$\bar{7},0,10$	<12	7	$\bar{9}36$	20	20
$\bar{6}03$	13	$\overline{10}$	$\bar{7},0,11$	17	11	$\bar{9}37$	12	18
$\bar{5}03$	<9	7	$\bar{7},0,12$	19	10	$\bar{9}38$	13	15
$\bar{4}03$	23	9	$\bar{7},0,13$	<14	14	$\bar{9}39$	15	14
$\bar{3}03$	9	$\overline{10}$	$\bar{7},0,14$	21	23	$\bar{9},3,10$	<10	4
$\bar{2}03$	28	$\overline{27}$				$\bar{9},3,11$	24	24
$\bar{1}03$	12	$\overline{15}$	$3,\bar{1},10$	13	10	$\bar{9},3,12$	22	21
300	26	$\overline{25}$	$3\bar{1}9$	26	22	$\bar{9},3,13$	12	15
103	8	11	$3\bar{1}8$	17	18	$\bar{9},3,14$	<13	10
203	9	$\bar{7}$	$3\bar{1}7$	9	6			
303	16	$\overline{17}$	$3\bar{1}6$	<7	6	$\overline{12},4,2$	16	15
			$3\bar{1}5$	19	39	$\overline{12},4,3$	25	18
$\bar{7}04$	24	22	$3\bar{1}4$	22	27	$\overline{12},4,4$	22	17
$\bar{6}04$	<9	6	$3\bar{1}3$	51	47	$\overline{12},4,5$	<12	1
$\bar{5}04$	<9	$\bar{1}$	$3\bar{1}2$	63	57	$\overline{12},4,6$	17	14
$\bar{4}04$	24	$\overline{20}$	$3\bar{1}1$	63	57	$\overline{12},4,7$	18	12
$\bar{3}04$	24	$\overline{25}$	$3\bar{1}0$	11	$\overline{14}$	$\overline{12},4,8$	19	14
$\bar{2}04$	8	$\bar{7}$	$\bar{3}11$	39	41	$\overline{12},4,9$	16	15
$\bar{1}04$	10	9	$\bar{3}12$	46	42	$\overline{12},4,10$	27	24
400	<8	$\bar{3}$	$\bar{3}13$	69	65	$\overline{12},4,11$	13	8
104	14	$\overline{22}$						

to facilitate this description each layer is considered in turn.

The mineral lithiophorite (LiAl)MnO$_2$(OH)$_2$ has a layer structure, in which the Mn atoms are each co-ordinated to six O atoms at the corners of a distorted octahedron which, sharing edges with six identical

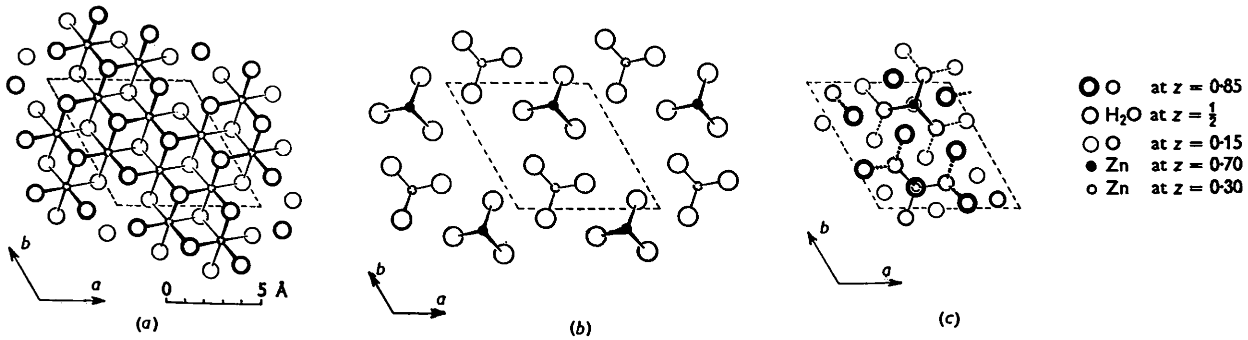


Fig. 5. (*a*) The MnO_6 layer viewed normal to the basal plane. The vacant octahedral sites at the origin are at the corners of a rhombus outlining the plane of the Mn atoms.

(*b*) The grouping of water molecules viewed normal to the plane at $z = \frac{1}{2}$. The Zn atoms are shown as smaller circles, the filled ones above, the open ones below the plane.

(*c*) The proposed system of hydrogen bonding (heavy broken lines) viewed normal to the plane at $z = \frac{1}{2}$.

In each case the broken lines outline a section of the unit cell.

ones, forms an infinite two-dimensional sheet (Wadsley, 1952). A similar layer of MnO_6 octahedra is found for chalcophanite except that every seventh metal site is vacant, causing a trigonal grouping of empty octahedral sites 7·54 Å apart (Fig. 5(*a*)). Mn_1 is coordinated to O_1, O_3 and O_4 in the plane at $z = 0{\cdot}15$ and to O_6, O_1 and O_2 at $z = -0{\cdot}15$; Mn_2 to O_2, O_4, O_5 and O_5, O_7, O_1; Mn_3 to O_3, O_5, O_6 and O_4, O_6, O_7. The atoms O_7, O_2, and O_3 in the two planes constitute the unoccupied octahedron. The O–O distances, taken from the sub-cell, are 2·85 Å for the unshared edges, and 2·65 and 2·68 Å for the shared edges. There is no evidence to indicate distances other than these in the octahedral edges of the vacant sites, since these are not foreshortened owing to sharing.

Zinc atoms are located above and below the vacancies in the manganese layer by bonds of length 1·93 and 1·98 Å to the oxygen atoms. Each zinc atom completes its coordination with three water molecules at distances 2·13 and 2·15 Å, so as to form an irregular octahedron.

The water molecules, all lying in the plane at $z = \frac{1}{2}$, are each distant 2·85 Å from five others. They are thus close packed with every seventh molecule absent, again leaving a trigonal grouping of unoccupied sites. This arrangement, best viewed normal to the plane of the water molecules (Fig. 5(*b*)), may be interpreted as triads of molecules grouped in open hexagon rings, each triad coordinated to a zinc atom, one at $z = 0{\cdot}30$, the adjacent ones at $z = 0{\cdot}70$. The projected view of this layer is strikingly similar to that of a layer of oxygen atoms in the structure of boric acid, H_3BO_3 (Zachariasen, 1934). In the case of chalcophanite, however, the triads are rotated by about 20°, nevertheless preserving the same double hexagon grouping. The layers each have hexagonal symmetry but are stacked in such a way that the unit cell, one axis of which links the vacant sites in the layers at $z = 0$ and $z = \frac{1}{2}$, becomes oblique. The strong pseudo-symmetry arises from the close packing of the layers, and with the zinc atom occupying only one of the several octahedral sites so formed. When viewed down the [130] and [510] axes, the vacancies in the manganese and water layers, as well as the zinc, appear to be distributed at random in the crystal structure as a whole, giving a prominent sub-cell. Such random groupings are a familiar feature in many mineral structures, and chalcophanite is notable amongst the complex manganese oxides for the resolution of the sub-cell components into a more ordered pattern.

The system of hydrogen bonding

The structure so far has been described in terms of the coordination of the metal atoms, and of the packing together of the individual layers. It is evident, however, that some additional binding forces in the crystal must exist, as the layers otherwise are held together by the close packing of the water molecules alone.

All attempts to develop a system of bonds by placing hydrogen atoms in the plane of the molecules, or

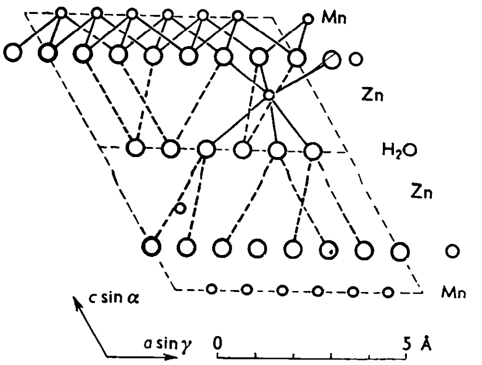
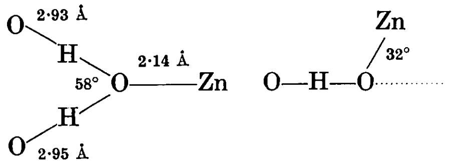


Fig. 6. The structure projected along the *b* axis. The heavy broken lines indicate the postulated hydrogen bridges between the layers. The other bonds in the upper half are the normal bonds between metal atoms, oxygens, and waters.

alternatively based upon the tetrahedral model of Bernal & Fowler (1933) led to inconsistencies. The most probable position of hydrogen bonds, assuming these to be localised, is shown in Figs. 5(*c*) and 6. Each water makes two external contacts with two oxygen atoms in the direction away from the zinc, $(H_2O)_1$ with O_5 and O_7, $(H_2O)_2$ with O_3 and O_6, $(H_2O)_3$ with O_1 and O_2; O_4 does not contribute to this scheme. The bond lengths and angles for each of the water molecules in coordination are identical, the H_2O–O distances being 2·93 and 2·95 Å, and the angle O–H_2O–O being 58°:



The three bonds from the water molecule are not coplanar, the Zn–H_2O bond making an angle of 32° with the plane of the atoms O–H_2O–O. This scheme closely resembles that for the hydrogen bridges in $Zn(BrO_3)_2.6H_2O$ (Yü & Beevers, 1936) except that for this compound the H_2O–O distance is shorter by 0·2 Å and the O–H_2O–O bonds are inclined at 121° to each other. Evidently the hydrogen bonds in chalcophanite are weak, and evidence to support this comes from the loss of most of the water when this mineral is heated to 140° C.

The coordination of the zinc atom

The zinc atom forms a curious coordination with the oxygens and waters. These are in octahedral grouping, but the Zn is not at the centre. The three bonds to oxygen, mutually inclined at 90±2°, are of mean length 1·95±0·5 Å, in good agreement with the value for zincite, ZnO, in which they are tetrahedral (Bragg, 1920). The bonds to the waters, inclined at 83±2°, and 2·15±0·05 Å in length, are similar to those in which zinc is octahedrally coordinated, to oxygen, as in smithsonite $ZnCO_3$ (Wells, 1950), or to water, as in $Zn(BrO_3)_2.6H_2O$ (Yü & Beevers, 1936). Neumann (1949), reviewing the mineralogy of zinc, has demonstrated that it is usually tetrahedrally coordinated but may also in certain cases form an octahedral configuration.

The bonds in chalcophanite obviously cannot be regarded as equivalent sp^3d^2 hybrids, and the more electronegative ligand groups, in this instance the water molecules, are believed to prefer *d* orbits to the others. This effect is probably common to other trihydrates, including that of zinc salicylate (Clarke, 1953), and a more detailed discussion has appeared elsewhere (Craig & Wadsley, 1954).

The evidence for interstitial ions

The chemical composition of chalcophanite differs appreciably from that calculated for the formula $ZnMn_3O_7.3H_2O$. It may contain significant amounts of lower-valency manganese, the number of cations usually exceeds four, and the water content, depending to a certain extent upon the analytical methods, may well be variable.

The recorded chemical analyses, recalculated on a basis of seven oxygen atoms, may be grouped as in Table 6. Here it will be seen that by raising the total of Mn^{4+} to three by including Mn^{2+} (or Fe^{2+}), the remaining Mn^{2+} (or Fe^{2+}), added to the Zn, are now in excess of one by an amount δ. For each case, this has a value which, perhaps fortuitously, is exactly identical with the amount of Mn^{2+} (or Fe^{2+}) added to the Mn^{4+}, so that the formula may be generalized as

Table 6. *Chemical data for chalcophanite*

	1		2		3		4	
Zn	1·07	1·22	1·03	1·14	0·92	1·25	0·91	
Mn^{2+}	0·15		0·11					
Fe^{2+}					0·33			
Mn^{4+}	2·78	3·00	2·86	3·00	2·76	3·00	3·04	3·05
Mn^{2+}	0·22		0·14				0·01	
Fe^{2+}					0·24			
O	7		7		7		7	
H_2O	2·6		2·8		2·7		2·9	
δ	0·22		0·14		0·25		0	
D(obs.)	3·90		—		4·01		3·70	
D(calc.)*	3·95		3·91		3·96		3·79	

Specimens 1, 2 and 3 from Sterling Hill, N.J., U.S.A. (*Dana's System of Mineralogy* (1944), vol. 1, p. 739). Specimen 4 from Buchan, Victoria, Australia (Wadsley, 1950).

* For *D*(calc.) it was assumed tha there are three molecules of water in the formula, rather than the fractional quantities in the table, which are considered unreliable. It was also assumed that the unit-cell volume for each was identical.

$$(Zn, Mn^{2+})_{1+\delta}(Mn^{4+}_{3-\delta}Mn^{2+}_{\delta})O_7.3H_2O\ ,$$

where δ may vary from 0 to 0·25.

If this is not due to chemical inaccuracy, a component with considerable scattering power is present for large values of δ. Assuming the additional ions to be Mn, a value of 0·25 will correspond to a peak of 5 electrons in the present investigation, and this should be resolved by X-ray methods if the intensities are sufficiently precise. It was considered that the small peak in the electron-density diagrams in the same plane as the zinc was due to these additional ions (Wadsley, 1953*b*, *c*). The height, estimated to be 3–4 e.Å^{-2}, corresponded to 0·2 Zn or Mn located at this point. The calculated density then became 3·95 g.cm.$^{-3}$, in much better agreement with the measured value, 3·98 g.cm.$^{-3}$, than that found with the stoichiometric formula.

There are four octahedral sites formed by the close packing of six waters and seven oxygens in the asymmetric unit of the structure. It has been seen that one is occupied by zinc; another, with the parameters (0·75, 0·80, 0·30), corresponds to the interstitial ions. Each of these latter forms three bonds to water molecules of mean length 2·15±0·05 Å, and three to oxygen ions 1·95±0·05 Å, and is thus identical with the Zn ion. Since the oxygens are already bonded to Mn^{4+}, however, a redistribution of the manganese valency electrons is necessary to preserve the balance of charge, and δ additional divalent ions between the oxygen and water sheets will give rise to an equal number in the Mn^{4+} layer. This type of electrical defect, here localized in the vicinity of the interstitial ions, is better known in the tungsten bronzes. It has been demonstrated for psilomelane (Wadsley, 1953*a*) and is believed to be common to many complex manganese oxides.

The octahedron coordinated to an additional ion shares an edge with a Zn octahedron and a face with the Mn octahedron immediately below. Chalcophanite specimens with appreciable values of δ probably represent a partial transition to another structural type. In order to avoid face sharing, a considerable regrouping of the Mn sheet must be made for a stoichiometric compound ($\delta = 1$) to have a stable configuration, and the prediction of this proposes many difficulties.

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References

Bernal, J. D. & Fowler, R. H. (1933). *J. Chem. Phys.* **1**, 515.
Bragg, W. L. (1920). *Phil. Mag.* (6), **39**, 647.
Clarke, G. L. (1953). Private communication.
Craig, D. P. & Wadsley, A. D. (1954). *J. Chem. Phys.* **22**, 346.
Dana's System of Mineralogy (1944), vol. 1, p. 739. New York: Wiley.
Frondel, C. (1953). Private communication.
International Tables for X-ray Crystallography (1952), vol. 1, § 2·5. Birmingham: Kynoch Press.
Moore, E. S. (1875). *Amer. Chem.* **6**, 1.
Neumann, H. (1949). *Miner. Mag.* **28**, 575.
Wadsley, A. D. (1950). *Amer. Min.* **35**, 485.
Wadsley, A. D. (1952). *Acta Cryst.* **5**, 676.
Wadsley, A. D. (1953*a*). *Acta Cryst.* **6**, 433.
Wadsley, A. D. (1953*b*). *Nature, Lond.* **172**, 1103.
Wadsley, A. D. (1953*c*). *Nature, Lond.* **172**, 1173.
Wells, A. F. (1950). *Structural Inorganic Chemistry*, p. 388. Oxford: Clarendon Press.
Yü, S. H. & Beevers, C. A. (1936). *Z. Kristallogr.* **95**, 426.
Zachariasen, W. H. (1934). *Z. Kristallogr.* **88**, 150.

Acta Cryst. (1955). **8**, 172

A Stencil Method for Computing Structure Factors

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A method of using the Donnay tables for the systematic computation of structure factors is described. The advantages of the method are that it is rapid, that the required apparatus is simple to construct, and that it makes use of existing tables. In addition, a complete record of the contribution of each atom to every structure factor is obtained.

Introduction

There is a need for a simple rapid method for calculating structure factors systematically, comparable with those available for summing Fourier series. The method proposed by Beevers & Lipson (1952) is a step in this direction, but its use is limited to the stages in a structure determination at which the atomic parameters can be expressed to the nearest 1/120th of the cell edge; the modification suggested for finer subdivision makes the method much more cumbersome. Strips with finer subdivision would be too extensive to produce *en masse*. Strips with fixed amplitude are quite practicable (Alexander, 1953), but require repetitive multiplication, a process that necessitates a calculating machine and is bound to slow down the calculations to some extent.

It occurred to the authors that it might be practicable to keep the apparatus within reasonable bounds by using stencils of the type employed in certain methods of Fourier synthesis (Patterson & Tunnell, 1942; Robertson, 1948). It was further discovered that cosine tables of the type required already existed in the form of those published by Donnay & Ham-