

to Fig. 3 (a) would account only for the maxima *A*, *B* and *D*, but leave *C* and *E* unexplained, all these maxima would be expected on assuming a type of structure shown in Fig. 3 (b). On the other hand, no unobserved maxima could be derived on that basis, whereas Fig. 3 (a) would demand maxima *F*, *G* and *H*.

The existence of seven layers seems more likely than of five, for in the latter case the side chains or haem groups would have to be responsible for the extension of the molecule in the *c'* direction being at least 56 Å. instead of about 42 Å.—the width of the five layers. The outline of the model represented by Fig. 4 is actually based on the assumption of seven layers.

It is possible to tackle the problem of the shape of the molecule from a different angle, starting from the above-mentioned hypothesis that short-range forces are keeping the molecules in position in the crystals at all states of swelling or shrinkage. The experimental data to be explained on this basis are the varying lattice constants of the dry, partly wet, wet and expanded crystals, as measured by Boyes-Watson *et al.* (1947, Tables 1 and 3, p. 93). They would be consistent with a cross-section of the molecule like the one shown in Fig. 4 in the arrangements it would assume in the dry,

normal wet, and expanded crystal. But this is not the only model consistent with these data. It should only serve as an example which seems preferable to all models suggested up to the present, in so far as it would be in keeping with (i) the one-dimensional Fourier projection (on *c'*) of the molecule, (ii) the Patterson projection (on the *b, c* plane) of the normal wet crystal, and (iii) the lattice constants of the various stages of swelling and shrinkage explained on the basis of short-range forces only. Further experimental data will have to be used to reject or confirm the outline of this model and, perhaps, to refine it.

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The Crystal Structure of Hollandite, the Related Manganese Oxide Minerals, and α - MnO_2

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Hollandite, cryptomelane, coronadite and α - MnO_2 form an isostructural series of the general formula $A_{2-y}B_{8-z}X_{16}$, *A* being large ions such as Ba^{2+} , Pb^{2+} , and K^+ , *B* small and medium-sized ions such as Mn^{4+} , Fe^{3+} , Mn^{2+} , and *X* in the cases investigated O^{2-} and OH^- ions. The unit cell, which contains one formula unit, is tetragonal or pseudotetragonal, in the latter case monoclinic. Approximate dimensions of the tetragonal unit cell are $a = 9.8$ and $c = 2.86$ Å. When deformed the short axis will be the *b* axis of the monoclinic cell. The deviation of β from 90° is $0.5\text{--}1.5^\circ$, and the difference $a - c$ is $0.1\text{--}0.2$ Å. The space group of the tetragonal cell is $C_{4h}^2\text{--}I4/m$ and the atomic positions are

$$\begin{aligned} (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + & \quad 2-y \text{ } A \text{ in } 2(b): \quad 0, 0, \frac{1}{2}; \\ & \quad 8-z \text{ } B \text{ in } 8(h): \quad x_1, y_1, 0; \bar{x}_1, \bar{y}_1, 0; \bar{y}_1, x_1, 0; y_1, \bar{x}_1, 0; \\ & \quad 8 \text{ } X \text{ in } 8(h): \quad \begin{cases} x_2, y_2, 0; \text{ etc.;} \\ x_3, y_3, 0; \text{ etc.} \end{cases} \end{aligned}$$

For a hollandite specimen the parameters were calculated to be

$$\begin{aligned} x_1 = 0.348, \quad x_2 = 0.153, \quad x_3 = 0.542, \\ y_1 = 0.167, \quad y_2 = 0.180, \quad y_3 = 0.167. \end{aligned}$$

The *A* ion is surrounded by eight oxygen ions at a distance of 2.74 Å. forming a cube and at a greater distance (3.31 Å.) by four oxygen ions forming a square at the same *z* level as the *A* ion. The *B* ion is surrounded by six oxygen ions forming an octahedron, and with a mean distance of $B\text{--}O = 1.98$ Å.

In the cases investigated, the variable *y* in the general formula varies from 0.8 to 1.3 and *z* from 0.1 to 0.5.

1. Introduction

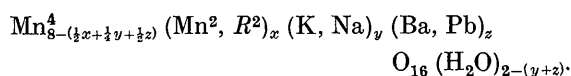
In the course of a study of manganese oxides, precipitates consisting of α - MnO_2 were obtained by the

reduction of a KMnO_4 solution by various reagents, for instance, H_2O_2 and HCl . As has been stated previously (Cole, Wadsley & Walkley, 1947), and as we could con-

firm, the X-ray powder photographs of these preparations showed that there must be a close structural similarity between α - MnO_2 and some of the manganese oxide minerals, namely, cryptomelane, hollandite and coronadite. The powder photographs of α - MnO_2 showed the characteristic broadening of the reflexions which is caused by very small crystallites. Heat-treated samples gave somewhat sharper reflexions, but it was impossible to obtain crystals large enough for rotation and Weissenberg methods. Hydrothermal syntheses also failed to produce such crystals. As no definite conclusions regarding the composition and structure of α - MnO_2 could be drawn from powder photographs alone, we determined to investigate also the above-mentioned manganese oxide minerals.

For the nomenclature of the manganese oxide minerals the rules recommended by Fleischer & Richmond (1943) have been applied. Their description of the chemical and X-ray characteristics of the minerals can be summarized as follows: The general formula is probably AR_8O_{16} with $A = \text{K, Pb and Ba}$, and $R = \text{Mn}^{4+}$ chiefly. The minerals contain 0–5% non-essential water. The symmetry is tetragonal (cryptomelane) or pseudotetragonal (coronadite and hollandite), in which case probably triclinic.

The size of the unit cell of cryptomelane has been determined by Ramsdell (1942) to be $a = 9.82, c = 2.86$ A. and by Richmond & Fleischer (1942) to be $a = 9.82, c = 2.83$ A. The reflexions indicate a body-centred cell. Frondel & Heinrich (1942) made unsuccessful efforts to index the powder patterns of coronadite and hollandite with this cell. However, they could index nearly all lines in terms of another body-centred tetragonal cell with $a = 6.95, c = 5.72$ A. for coronadite and $a = 6.94, c = 5.71$ A. for hollandite. For coronadite they suggested the formula $\text{MnPbMn}_6\text{O}_{14}$ or $\text{MnPbMn}_6\text{O}_{14}\text{H}_2\text{O}$. Hollandite was looked upon as the barium analogue of coronadite, perhaps $(\text{MnFe})\text{BaMn}_6\text{O}_{14}$. As will be seen, there is a close relationship between the unit cell of cryptomelane and that suggested for hollandite and coronadite: $6.95\sqrt{2} = 9.82$ and $5.72/2 = 2.86$. Richmond & Fleischer (1942) remark that the powder and Weissenberg photographs of cryptomelane and hollandite are nearly identical and suggest that the three minerals are isostructural. Gruner (1943) assumes a complicated general formula for the three minerals, namely,



2. Unit cell and formula of hollandite

During an investigation of Swedish manganese ores by Ödman (1947) a number of mineral specimens were collected, which, by X-ray powder photographs, were shown to belong to the hollandite–coronadite–cryptomelane isostructural series. From these specimens a number of prismatic crystals were selected, and rotation and Weissenberg photographs were taken with the

prism axis as rotation axis. All rotation photographs showed a period of about 2.85 A. in this direction.

However, the Weissenberg photographs differed considerably. For a crystal picked out from hollandite I (see below), the Weissenberg photographs showed the tetragonal Laue symmetry C_{4h} with $a \doteq 9.9$ A. The powder photographs could not be indexed with a tetragonal cell. Several reflexions were split, but this could be accounted for if a small monoclinic deformation was assumed with the tetragonal c axis as b axis in this monoclinic cell. In other cases, the Weissenberg photographs also showed the lower symmetry, but then the crystals always consisted, not of one individual only, but of two or more. In the case of hollandite II, there appears a very weak reflexion in the powder photographs at a slightly larger glancing angle than 020 (Table 4). This reflexion cannot be indexed with the same cell as the other reflexions. It seems probable that it indicates the presence of another hollandite phase in this specimen with a slightly smaller b axis (2.857 instead of 2.875 A.). For all reflexions with $k=1$ this difference in b axis will make a very small difference in glancing angle (0.0020 in the value of $\sin^2\theta$), and as all the reflexions in these photographs are broadened, a further splitting of the reflexions due to the presence of another phase will be impossible to recognize. However, from the relative intensities of the two 020 reflexions it seems that this other phase is present in an amount of about 10–20%. For hollandite I and for the main constituent in hollandite II the following cell dimensions are obtained from the powder photographs (Cr $K\alpha = 2.2909$ A.):

Hollandite I (162/43)	Hollandite II (294/43)
$a = 9.91 \pm 0.01$ A.	$a = 10.00 \pm 0.01$ A.
$b = 2.872 \pm 0.003$ A.	$b = 2.879 \pm 0.003$ A.
$c = 9.75 \pm 0.01$ A.	$c = 9.72 \pm 0.01$ A.
$\beta = 90.6^\circ$	$\beta = 91.1^\circ$
$V = 278.0$ A. ³	$V = 278.8$ A. ³

The reflexions of the powder photographs are listed in Table 4.

Analyses on carefully selected material were carried out by A. Bygdén. The coarse material was washed with SO_2 water and dilute HCl (room temperature) to dissolve the pyrolusite from the surface of the material used for analyses, whereafter particles with a specific gravity less than 3.94 were separated with Clerici solution. These particles amounted to about 0.15% of the original sample. The analyses are given in Table 1. In Table 2 the number of atoms are calculated with the assumption of 16 oxygen ions + hydroxyl ions in the unit cell.

For the chief metal components the following ionic radii are valid:

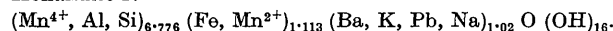
Mn^{4+} 0.50 A.	Fe^{3+} 0.60 A.	Na^+ 0.95 A.	Ba^{2+} 1.35 A.
Al^{3+} 0.50 A.	Mn^{2+} 0.80 A.	K^+ 1.33 A.	Pb^{2+} 1.21 A.

Apparently the true oxidation state of the elements in the minerals cannot be deduced from the analyses. From

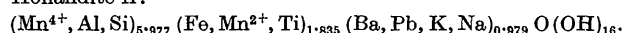
the fact that hollandite and coronadite are isostructural, it seems safe to deduce that the lead is present as Pb^{2+} ions. It seems reasonable to assume that in a mineral with Mn^{4+} as dominating component, iron is present as Fe^{3+} ions. The manganese atoms are given as Mn^{4+} ions and Mn^{2+} ions. This is obviously quite arbitrary; they could as well be divided into Mn^{4+} and Mn^{3+} ions, the

latter with an ionic radius of 0.62 Å. If the ions are divided into three groups, small, medium-sized, and large ions, the following formulas for the cell contents are obtained:

Hollandite I:



Hollandite II:



With these cell contents, the specific gravities were calculated to be 4.721 and 4.884 respectively, as compared with the experimental values of 4.705 and 4.964.

Table 1. *Analyses of two hollandites from the Ultevis district, Sweden*

(Analyst A. Bygdén.)

	Hollandite I (%)	Hollandite II (%)
SiO_2	0.09	0.20
TiO_2	0.03	0.38
Al_2O_3	1.69	0.63
Fe_2O_3	6.44	12.52
MnO	62.18	54.49
BaO	9.14	14.28
PbO	3.25	4.32
Na_2O	0.43	0.05
K_2O	1.96	0.22
$\text{H}_2\text{O} < 105^\circ \text{C.}$	0.06	0.09
$\text{H}_2\text{O} > 105^\circ \text{C.}$	1.00	1.35
O	13.14	11.32
S	0.01	0.02
Insoluble in 20% HCl	0.18	0.19
	99.60	100.06

Hollandite I: labelled Ö 162/43, Sörhåras, Ultevis, Jokkmokk.

Hollandite II: labelled Ö 294/43, Stuur Njuoskes, Ultevis, Jokkmokk.

$\text{CoO} = 0.012\%$ and $\text{CuO} = 0.014\%$. NiO , CaO and MgO are not present in quantities enough for gravimetric analysis on 1 g material.

3. Symmetry, space group and structure of hollandite

As was mentioned previously, some Weissenberg photographs showed the tetragonal symmetry C_{4h} , whereas others indicated a monoclinic unit cell. In the following, indices referring to a tetragonal cell are denoted with the subscript t , and those referring to a monoclinic cell with the subscript m . The axis of the two cells are related in the following way:

$$a_t = a_m, \quad b_t = c_m \quad \text{and} \quad c_t = b_m.$$

In all the Weissenberg photographs only reflexions with $h+k+l=2n$ appeared. No special space-group criteria were valid. Possible space groups in the tetragonal system are C_{4h}^5-I4/m , C_4^2-I4 and S_4^2-I4 , and in the monoclinic system C_{2h}^3-I2/m , C_2^2-I2 and C_2^3-Im . The monoclinic deformation is very small, and therefore it is justified to assume the same atomic arrangement as

Table 2. *Calculated atomic contents and densities of unit cell based on (a) $(\text{O} + \text{OH} = 16)$ and (b) $\text{O} = 16$*

	Hollandite I		Hollandite II		Coronadite 5		Cryptomelane 1	
	a	b	a	b	a	b	a	b
Mn^{4+}	6.47	6.66	5.85	6.06	6.28	6.66	6.83	7.30
Mn^{2+}	0.477	0.490	0.500	0.520	1.04	1.10	0.209	0.224
Ba	0.469	0.483	0.769	0.800	0.013	0.014	0.006	0.006
Ca	—	—	—	—	0.008	0.008	0.034	0.036
Mg	—	—	—	—	—	—	0.008	0.009
Pb	0.115	0.118	0.159	0.165	1.18	1.25	—	—
Zn	—	—	—	—	—	—	0.459	0.492
Cu	—	—	0.002	0.002	0.016	0.017	0.010	0.011
Na	0.109	0.112	0.013	0.013	—	—	0.102	0.109
K	0.328	0.338	0.038	0.040	—	—	0.523	0.565
Al	0.260	0.268	0.100	0.105	0.018	0.019	0.053	0.057
Fe	0.636	0.654	1.30	1.35	0.070	0.075	0.041	0.043
Si	0.013	0.013	0.027	0.028	0.04	0.04	0.068	0.073
Ti	—	—	0.039	0.040	—	—	0.001	0.001
ΣP, As, V	—	—	—	—	0.02	0.02	0.007	0.007
H_2O^+	0.437	0.450	0.619	0.645	0.916	0.972	1.02	1.09
O	15.56	16.00	15.38	16.00	15.08	16.00	14.98	16.00
Cations	8.88	9.14	8.80	9.13	8.69	9.20	8.35	8.93
Mol. wt.	784	806	824	856	913	970	713	762
Cell vol. (Å. ³)	275.7	—	278.5	—	278.4	—	275.1	—
Sp.gr. calc.	4.72	4.85	4.88	5.07	5.42	5.74	4.27	4.56
Sp.gr. obs.	4.705	—	4.964	—	5.44	—	4.33	—

Hollandite I and Hollandite II, see Table 1 this paper.

Coronadite 5 from Bou Tazoult, Morocco. Analysis from paper by Lindgren (1933). Cell dimensions determined from powder photographs with focusing cameras from a specimen presented to the Mineralogical Institute of the University of Stockholm by Muséum National d'Histoire Naturelle, France.

Cryptomelane 1 from Tombstone, Arizona. Analysis from a paper by Richmond & Fleischer (1942). Cell dimensions are determined from a specimen presented to the Geological Survey of Sweden by Mr Fleischer.

The numbers 5 for coronadite and 1 for cryptomelane are retained for comparison of the same minerals in papers by Frondel & Heinrich, and Gruner respectively.

in the tetragonal cell, which gives the following intensity relations:

$$I(h_m k_m l_m) = I(\bar{l}_m k_m h_m), \text{ and } I(h_m k_m \bar{l}_m) = I(l_m k_m h_m).$$

In fact, a very well-exposed zero-layer line of a monoclinic crystal showed only small deviations from these intensity relations.

The intensities used for the structure determination were taken from Weissenberg photographs (Cr *K* radiation) of a crystal picked out from the specimen hollandite I (see Tables 1 and 2). In spite of the fact that the powder photographs showed a monoclinic deformation of the unit cell, the Weissenberg photographs did not show any deviation from tetragonal symmetry, and the precision of the camera was certainly sufficient to show the difference of length between a_m and c_m . However, weak additional reflexions indicate the presence of the monoclinic phase, and in view of the fact that the reflexions from both have the same relative intensity, the analysis used is assumed to be valid for either.

In the estimation of the intensities the relation $I_\alpha/I_\beta=7$ was used. The intensity of 440 was arbitrarily taken as 100. From the estimated values of I , $|F|_{\text{obs.}}$ was calculated by the formula $|F|_{\text{obs.}} = \left\{ I \sin \gamma \frac{2}{\cos^2 2\theta} \right\}^{\frac{1}{2}}$ (Kaan & Cole, 1949). All the $|F|_{\text{obs.}}$ values were then multiplied by a constant to make the sum of the positive and negative values of $|F|_{\text{obs.}} - |F|_{\text{calc.}}$ close to zero. No attempt at timing the photographs of different levels was made. As barium and manganese are the main constituents, the scattering factors of the other metallic elements were recalculated in terms of f_{Ra} and f_{Mn} respectively.

From the formula of hollandite I (see above) it appears that there are 8.9 metal ions and 16 oxygen + hydroxyl ions to place in the unit cell. As the structure is body-centred there must be an even number of atomic sites in the cell, and it seems most probable that the metal ions are distributed over ten sites. In C_{4h}^5-I4/m there are two ways of combining the positions to give ten sites, either one twofold position + two fourfold positions or one twofold + one eightfold position. Only the possibilities 2 (*a*) or 2 (*b*) + 8 (*h*) lead to reasonable interatomic distances.

Now it seems more probable that Ba^{2+} , K^+ , Na^+ and Pb^{2+} ions—in all 1.02 in the cell—are placed in 2 (*a*) or 2 (*b*) and the rest of the metal ions—in all 7.86—in 8 (*h*), than to fill up 2 (*a*) or 2 (*b*) with Mn^{2+} or Fe^{3+} and place the rest of the ions—6.88—in 8 (*h*), as the difference in size between Ba^{2+} and Mn^{2+} (the largest of the medium-sized ions) is nearly twice the difference between Mn^{2+} and Mn^{4+} . The following arrangement of the metal ions is then arrived at:

$$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$$

1.02 (Ba, K, Na, Pb) in 2 (*a*) or 2 (*b*): 0, 0, 0 or 0, 0, $\frac{1}{2}$;

7.86 (Mn, Fe, Al, Si) in 8 (*h*): $x, y, 0; \bar{x}, \bar{y}, 0; \bar{y}, x, 0; y, \bar{x}, 0$.

A rough variation of the parameters showed that with $2\pi x_1 = 115-125^\circ$ and $2\pi y_1 = 55-65^\circ$ and the large atoms in 2 (*b*), most of the calculated F values agreed with those observed (compare columns 1 and 2 in Table 5). The other two possible tetragonal space groups C_{4h}^5-I4 and S_4^2-I4 gave no further alternative for the arrangement of the metal ions in the x, y plane. However, there appear some rather large discrepancies: the calculated F value of 330 is very much too high and that of 301 too low, 420 should be weaker than 240 but is stronger, and 820 should be weaker than 280 and not stronger as calculated; but the oxygen atoms can be expected to have a rather large influence on the F values.

An inspection of the available space shows that the 16 oxygen + hydroxyl ions can be arranged in two fundamentally different ways, either in planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ forming a three-dimensional tetrahedron framework around the ions in 8 (*h*), or at $z = 0$ and $z = \frac{1}{2}$ forming a three-dimensional octahedron framework. With the former alternative $F(002) = 77$ and with the latter $F(002) = 192$. From a Weissenberg photograph of the hhl reflexions it appeared that 002 was one of the strongest reflexions, much stronger than 660 with $F \doteq 100$, and that speaks definitely in favour of the alternative with octahedron framework, corresponding in C_{4h}^5 to an arrangement with 16 oxygen + hydroxyl ions in 2.8 (*h*) with the approximate parameters $2\pi x_2 \doteq 60^\circ$, $2\pi y_2 \doteq 60^\circ$, $2\pi x_3 \doteq 180^\circ$ and $2\pi y_3 \doteq 60^\circ$. A careful variation of all the parameters around the approximate values leads to the following structure:

Space group C_{4h}^5-I4/m

1.02 (Ba, Pb, K, Na) in 2 (*b*).

7.86 (Mn, Fe, Al, Si) in 8 (*h*):

$$\begin{aligned} 2\pi x_1 &= 125^\circ \pm 2^\circ, & x_1 &= 0.348 \pm 0.005, \\ 2\pi y_1 &= 60^\circ \pm 2^\circ, & y_1 &= 0.167 \pm 0.005. \end{aligned}$$

16 (O + OH) in 2.8 (*h*):

$$\begin{aligned} 2\pi x_2 &= 55^\circ \pm 3.5^\circ, & x_2 &= 0.153 \pm 0.010, \\ 2\pi y_2 &= 65^\circ \pm 3.5^\circ, & y_2 &= 0.180 \pm 0.010, \\ 2\pi x_3 &= 195^\circ \pm 3.5^\circ, & x_3 &= 0.542 \pm 0.010, \\ 2\pi y_3 &= 60^\circ \pm 3.5^\circ, & y_3 &= 0.167 \pm 0.010. \end{aligned}$$

As will be seen from Table 5, the agreement between observed and calculated intensities is very satisfactory. The correctness of the oxygen positions is proved both by the disappearance of all the discrepancies mentioned above and by the fact that the quotient

$$\frac{\sum ||F|_{\text{obs.}} - |F|_{\text{calc.}}|}{\sum |F|_{\text{obs.}}}$$

is decreased from 0.29 to 0.19 when reckoning with the oxygen atoms.

4. Discussion of the structure

With the above-mentioned parameter values the following interatomic distances are obtained. (In these calculations the dimensions from the Weissenberg photo-

graphs $a_t = 9.96 \pm 0.05$ and $c_t = 2.86 \pm 0.01$ A. were used):

In the same plane	In different planes
4 (Ba-O ₂) = 3.31 A.	8 (Ba-O ₁) = 2.74 A.
1 (Mn-O ₁) = 1.94 A.	2 (Mn-O ₁) = 2.12 A.
1 (Mn-O ₂) = 1.93 A.	2 (Mn-O ₂) = 1.90 A.
1 (O ₁ -O ₁) = 3.33 A.	2 (O ₁ -O ₁) = 2.78 A.
1 (O ₂ -O ₂) = 3.44 A.	2 (O ₂ -O ₂) = 2.81 A.
1 (O ₁ -O ₂) = 3.88 A.	2 (O ₁ -O ₂) = 2.61 A.
1 (O ₂ -O ₁) = 2.77 A.	2 (O ₂ -O ₁) = 2.86 A.
	2 (Mn-Mn) = 2.93 A.

Further, there are the distances Ba-Ba, Mn-Mn, O-O equal to c (= 2.86 A.).

As will be seen from Fig. 1, the oxygen and hydroxyl ions form octahedra around the manganese ions. As in ramsdellite (Byström, 1949) these octahedra are linked together to form double strings running in the c direction, the octahedra in one string sharing an edge with two consecutive octahedra from the other string. In each string the octahedra share opposite edges in the c direction. The double strings are combined to a three-dimensional framework by sharing corners. The large ions at $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$ are surrounded by eight O₁ ions, situated at the corners of a slightly distorted cube with $M-O = 2.74$ A., and four O₂ ions at 3.31 A., the latter at the corners of a square, which is perpendicular to the c axis and bisects the sides of the cube. The sum of the bond strengths is 2.0 for the O₁ ions and 1.9 for the O₂ ions, in very good agreement with expected values.

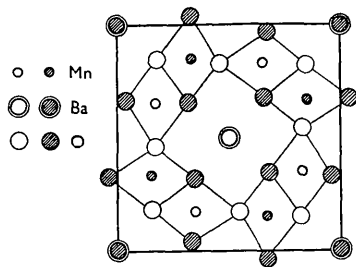


Fig. 1. The structure of hollandite projected on (001). Open circles denote ions at the level $z=0$ and filled circles ions at the level $z=\frac{1}{2}$.

The mean distance Mn-O is 1.98 A. In the two modifications of MnO₂, whose structures have hitherto been determined, pyrolusite and ramsdellite, the Mn-O distances are slightly shorter, being 1.88 A. for pyrolusite and 1.89 A. for ramsdellite, but then the amount of lower-valency ions in hollandite (Fe³⁺, Mn²⁺) must cause an increase of these distances. The increase is larger than expected, but this may be owing to parameter errors.

However, the most peculiar feature in the hollandite structure is doubtless the short Ba-Ba distances of 2.86 A., i.e. only a little more than twice the ionic radius of the Ba²⁺ ion. Now it is true that the position 2(*b*) is only filled to 50%, but there is still a possibility of 25% for Ba ions in adjacent positions. It seems that an arrangement with half as many atomic sites but all

filled in a larger unit cell would be preferable. This is possible in a primitive cell with the c axis 2×2.86 A., but in none of the rotation photographs of different hollandites is there any indication of an extra layer line nor any reflexions with $h+k+l=2n+1$. Thus it can be stated that the former arrangement with short Ba-Ba distances statistically in every fourth cell is preferable. These short Ba-Ba distances may be one of the reasons why the hollandite structure always seems to have a tendency to disorder, manifested by the fact that the reflexions in the powder photographs are broadened, which is also the case for cryptomelane. Only for coronadite with somewhat smaller Pb²⁺ ions are powder photographs of normal sharpness obtained. That the large ions are loosely bound is also demonstrated by the fact that the α -MnO₂ preparations show cation exchange like the zeolite minerals (Gruner, 1943). This will be discussed in a later section.

Besides the positions occupied by the barium and manganese ions in hollandite there are possible metal atom sites at $0, \frac{1}{2}, z$ and $\frac{1}{2}, 0, \bar{z}$. With $z = \frac{1}{4}$ these positions are surrounded tetrahedrally by four oxygen ions at 1.8 A. (There are such holes at both $z = \frac{1}{4}$ and $z = \frac{3}{4}$, but the $M-M$ distance would be only $\frac{1}{2}c = 1.43$ A., which seems improbably short.) The distance to adjacent Mn ions would be 2.2 A., a rather short distance, but not impossible. However, careful intensity calculations indicate that these positions are not occupied in hollandite.

5. The monoclinic cell of hollandite

As was shown above, the powder photographs indicate that the unit cell of hollandite is often slightly deformed to monoclinic symmetry. The structure can be described in C_{2h}^3-I2/m with the barium ions in 2(*b*) and the manganese ions and the oxygen ions in 4(*i*). Because of the small deviation from tetragonal symmetry (see above), it is possible to give correct signs to nearly all the structure factors. A Fourier analysis can then be carried out to show how the parameters should be adjusted. This will be discussed in a later paper.

6. Cryptomelane and coronadite

Powder photographs of cryptomelane from Tombstone, Arizona, and coronadite from Bou Tazoult, Morocco, showed no deviations from tetragonal symmetry. The cell dimensions were calculated to be

$$a = 9.84, \quad c = 2.858 \text{ A. for cryptomelane}$$

$$\text{and } a = 9.89, \quad c = 2.862 \text{ A. for coronadite.}$$

As will be seen from Table 2 the agreement between observed densities and those calculated with 16 (O + OH) ions in the cell is very good. The statement that these specimens are both tetragonal is obviously true within the limits of the resolving power of the powder cameras. The photographs were taken with focusing cameras of Phragmén type. The maximum difference in length between a_t and b_t (or rather a_m and c_m if a difference

really exists) is for cryptomelane about 0.02 Å. and for coronadite 0.005–0.01 Å. The deviation of the angle from 90° is in the former case $\leq 0.3^\circ$ and in the latter case $\leq 0.1^\circ$.

7. The general formula of the minerals

The general formula $A_{2-y}B_{8-z}X_{16}$, is apparently suggested by the structure.* A represents large ions (Ba^{2+} , Pb^{2+} , K^+ , Na^+ chiefly) and B small ions, chiefly Mn^{4+} , which to balance the formula is substituted by ions like Fe^{3+} , Mn^{2+} (or Mn^{3+}), Zn^{2+} . y is always approximately unity in the minerals hitherto investigated, and must probably be so at least in the barium and potassium compounds because of the short $A-A$ distances (see above). In the four minerals discussed here, z falls within the limits 0.1–0.5. X represents anions which are O or OH in the minerals of this series here investigated, the amount of OH ranging from 5 to 12 % in the minerals hitherto discussed. Of other anions F⁻ is of the size to be accommodated in these positions.

From Gruner's general formula it follows that there are sixteen oxygen ions in the cell and that the number of water molecules + number of Ba, Pb, K, Na ions is two, thus indicating that the water molecules (the H_2O^+ water in the analyses) and the large ions together occupy a twofold position. This assumption leads to a different formula for the minerals (Table 2), but the difference is too small to affect the intensities measurably. However, H_2O molecules in the same position as the barium atoms in hollandite would give eight O– H_2O distances of 2.74 Å. These short distances must imply hydrogen bonding, but there are only two hydrogen atoms, which thus must be distributed among eight bonds. It seems that in such a case longer O–H–O distances would be expected, as the O–H–O distance in diaspore (Ewing, 1935), with one bond per hydrogen atom, is 2.65 Å., thus only slightly shorter, whereas in ramsdellite (Byström, 1949), without hydrogen bonds, but with the same structure, the O–O distance is increased to about 3.3 Å. It may also be pointed out that in the zeolites (according to Gruner the water in cryptomelane is of zeolitic nature) the water molecules are surrounded by only two oxygen ions or other water molecules and one or two positive ions (Bragg, 1937).

Gruner has shown that his formula gives fairly good agreement between observed and calculated densities. In these calculations he has, however, omitted the water in the analyses, in spite of the fact that he declares that only a small part of it can be adsorbed. We have recalculated the densities with his formula, including the water, and the results are shown in Tables 2 and 3. The

difference $\{(d_{\text{calc.}} - d_{\text{obs.}})/d_{\text{obs.}}\} \times 100$ is shown below for the two alternatives:

		Hollandite I	Hollandite II
Diff. Gruner	(%)	3.1	2.1
Diff. Byström	(%)	0.3	-1.7
		Coronadite	Cryptomelane 1
Diff. Gruner	(%)	5.2	5.3
Diff. Byström	(%)	-0.4	-1.4

For the specimens in Table 3 we have not, because of lack of material, been able to control the cell dimensions, but have taken values from comparable minerals with the following results:

		Hollandite (Kajlidongri)	Coronadite	
Diff. Gruner	(%)	2	7	
Diff. Byström	(%)	2	3.4	
		Cryptomelane		
		2	3	4
Diff. Gruner	(%)	1.8	2.7	7.7
Diff. Byström	(%)	-2.3	-6	-3.1

As will be seen, Gruner's formula leads to a larger difference between observed and calculated densities in six out of nine cases and to better agreement in only one case. As also structural reasons make Gruner's hypothesis for the water distribution suspicious, it seems that our suggestion with the water as hydroxyl ions among the oxygen ions is the correct one. However, it is possible that in several cases (those with larger observed than calculated densities) part of the water present is adsorbed, which would lead to higher calculated densities.

Just those specimens for which the differences $d_{\text{calc.}} - d_{\text{obs.}}$ are negative and large, are optically isotropic and give broadened X-ray reflexions. This hints that the crystallites are of the dimensions $< (1000)^3 \text{ Å}^3$. If we assume that one water molecule can be adsorbed by each ion on the surface of the crystallites (H_2O being a dipole), the amount of the adsorbed water for $V \sim 1000^3 \text{ Å}^3$ will be approximately 1 %. If the crystallites are only 500^3 Å^3 , approximately 2 % H_2O can be adsorbed. The calculated densities agree with those observed for cryptomelane 2, 3 and 4 if we assume that 50, 70 and 40 % respectively of the water (H_2O^+) is present as adsorbed water, corresponding in weight percentages to 0.9, 2.3 and 1.3 %. As will be seen, the crystallites in the specimen cryptomelane 2 must be very small to allow such an adsorption. Apparently, the presence of such an adsorbed layer of water on the surfaces of the crystallites does not prevent the specimens from looking massive and compact. Included water may influence the results, but it seems that water of that type must be driven off at temperatures below 110° C., and here only H_2O^+ water is discussed.

As is shown in Table 3, the sum of numbers of Al, Mn and Fe ions in the hollandite from Kajlidongri is larger than eight (8.46). It is rather improbable that the surplus of these ions would occupy the vacant sites in

* An extension of the general formula is possible if the tetrahedral atomic sites discussed in the previous section are filled. If C represents small ions with radius 0.4 Å., the formula will be: $A_{2-y}B_{8-z}C_{2-u}X_{16}$.

Table 3. Calculated atomic contents and densities of unit cells based on (a) (O+OH=16) and (b) O=16

(Cell dimensions taken from corresponding minerals, with unit cell determined.)

	Hollandite Kajlidongri		Coronadite 6		Cryptomelane							
					2		3		4			
	a	b	a	b	a	b	a	b	a	b	a	b
Mn ⁴⁺	6.54	6.54	6.47	6.70	7.20	7.53	6.56	7.16	6.80	7.57	6.80	7.57
Mn ²⁺	0.62	0.62	0.92	0.96	0.40	0.42	0.34	0.37	0.24	0.26	0.24	0.26
Ba	1.00	—	—	—	0.05	0.05	—	—	—	—	—	—
Pb	—	—	1.19	1.23	—	—	—	—	—	—	—	—
Na	—	—	—	—	0.11	0.11	0.13	0.14	0.11	0.12	0.11	0.12
K	—	—	—	—	0.60	0.62	0.57	0.62	0.45	0.50	0.45	0.50
Al	0.15	0.15	0.12	0.13	—	—	0.19	0.20	0.05	0.06	0.05	0.06
Fe	1.15	1.15	0.13	0.13	0.02	0.02	0.35	0.38	0.01	0.01	0.01	0.01
RO	—	—	0.01	0.01	0.09	0.06	0.18	0.19	0.15	0.17	0.15	0.17
H ₂ O ⁺	None	None	0.57	0.58	0.65	0.71	1.34	1.47	1.35	1.50	1.35	1.50
O	16.00	16.00	15.43	16.00	15.35	16.00	14.66	16.00	14.65	16.00	14.65	16.00
Cations	9.46	9.46	8.84	9.16	8.47	8.81	8.32	9.06	7.81	8.69	7.81	8.69
Mol. wt.	854	854	918	952	704	735	693	756	673	750	673	750
Cell vol. (A. ³)	278	278	278.4	278.4	275.5	275.5	275.5	275.5	275.5	275.5	275.5	275.5
Sp. gr. calc.	5.05	5.05	5.43	5.62	4.22	4.40	4.16	4.53	4.04	4.49	4.04	4.49
Sp. gr. obs.	4.95	4.95	5.25	5.25	4.32	4.32	4.41	4.41	4.17	4.17	4.17	4.17

The values given in columns (b) are taken from Table 3 in a paper by Gruner (1943) with the exception of the molecular weights to which water is added.

Hollandite from Kajlidongri, India. Analysis from a paper by Frondel & Heinrich (1942).

Coronadite 6 from Coronado vein, Clifton Morenci, Arizona. Analysis from Frondel & Heinrich (1942).

Cryptomelane 2, 3, 4. Analysis from Richmond & Fleischer (1942).

Table 4. Powder photographs of hollandite I and hollandite II

CrK radiation. β -reflexions are omitted, but when coinciding with α reflexions, $I_{obs.}$ is marked with an asterisk.

Hollandite I					Hollandite II				
$d_{obs.}$ (kX.)	$\sin^2 \theta_{obs.}$	$\sin^2 \theta_{calc.}$	hkl	$I_{obs.}$	$d_{obs.}$ (kX.)	$\sin^2 \theta_{obs.}$	$\sin^2 \theta_{calc.}$	hkl	$I_{obs.}$
3.500	0.1066	0.1073	202	<i>m.</i>	3.525	0.1051	0.1060	202	<i>st.</i>
3.465	0.1088	0.1097	20 $\bar{2}$	<i>v.w.</i>	3.463	0.1089	0.1090	20 $\bar{2}$	<i>st.*</i>
3.128	0.1334	{0.1315	301}	<i>st.</i>	3.170	0.1293	0.1300	301	<i>st.</i>
		{0.1333	30 $\bar{1}$ }		3.134	0.1323	0.1330	30 $\bar{1}$	<i>v.st.</i>
3.105	0.1354	{0.1362	103}	<i>st.</i>	3.105	0.1354	0.1360	103	<i>v.st.</i>
		{0.1382	10 $\bar{3}$ }		3.070	0.1386	0.1390	10 $\bar{3}$	<i>st.</i>
2.757	0.1719	{0.1721	110}	<i>w.</i>	2.741	0.1746	{0.1731	110}	<i>v.w.</i>
		{0.1732	011}				{0.1738	011}	
2.477	0.2127	0.2126	400	<i>w.+</i>	2.700	0.1790	—	?	<i>w.</i>
2.440	0.2194	0.2204	004	<i>w.</i>	2.496	0.2095	{0.2093	400}	<i>m.</i>
2.399	0.2271	{0.2271	21 $\bar{1}$ }	<i>st.*</i>			{0.2211	004}	
		{0.2264	112}		2.406	0.2256	0.2261	211	<i>st.*</i>
2.196	0.2708	{0.2704	40 $\bar{2}$ }	<i>v.st.</i>	2.336	0.2391	0.2383	303	<i>v.w.</i>
		{0.2714	204}		2.234	0.2615	0.2615	402	<i>w.</i>
2.163	0.2791	0.2792	310	<i>st.</i>	2.198	0.2703	{0.2690	40 $\bar{2}$ }	<i>st.</i>
2.149	0.2827	0.2831	013	<i>st.</i>			{0.2704	204}	
1.978	0.3338	0.3326	312	<i>w.</i>	2.172	0.2768	{0.2784	204}	<i>st.</i>
1.963	0.3389	0.3383	21 $\bar{3}$	<i>w.</i>			{0.2759	310}	
1.941	0.3465	0.3459	501	<i>m.—</i>	2.146	0.2834	0.2828	013	<i>st.</i>
1.914	0.3566	0.3563	105	<i>m.—</i>	1.993	0.3289	0.3285	312	<i>w.*</i>
1.838	0.3867	{0.3842	411}	<i>st.</i>	1.964	0.3385	{0.3383	21 $\bar{3}$ }	<i>m.</i>
		{0.3867	41 $\bar{1}$ }				{0.3388	501}	
1.823	0.3926	{0.3917	114}	<i>st.</i>	1.897	0.3628	0.3626	105	<i>v.w.*</i>
		{0.3941	11 $\bar{4}$ }		1.856	0.3799	0.3795	411	<i>st.</i>
1.744	0.4295	0.4290	404	<i>w.</i>	1.844	0.3838	0.3835	41 $\bar{1}$	<i>m.</i>
1.727	0.4380	0.4370	404	<i>w.</i>	1.825	0.3920	0.3910	114	<i>m.</i>
1.684	0.4600	0.4622	50 $\bar{3}$	<i>m.*</i>	1.817	0.3954	0.3951	11 $\bar{4}$	<i>st.</i>
1.648	0.4805	{0.4806	600}	<i>st.</i>	1.755	0.4240	0.4236	404	<i>w.</i>
		{0.4828	510}		1.723	0.4399	0.4396	404	<i>w.</i>
1.623	0.4960	0.4961	006	<i>st.</i>	1.664	0.4717	0.4716	600	<i>st.</i>
1.547	0.5458	0.5450	512	<i>w.</i>	1.618	0.4991	{0.4973	41 $\bar{3}$ }	<i>br.m.</i>
1.540	0.5498	0.5509	512	<i>st.</i>			{0.4996	006}	
1.536	0.5533	0.5540	215	<i>st.</i>	1.562	0.5358	0.5359	512	<i>w.</i>
1.527	0.5588	0.5600	21 $\bar{5}$	<i>w.</i>	1.547	0.5453	0.5459	51 $\bar{2}$	<i>st.</i>
1.432	0.6366	0.6364	020	<i>m.</i>	1.537	0.5533	0.5534	215	<i>st.</i>
1.416	0.6516	0.6532	121	<i>v.w.</i>	1.525	0.5618	0.5634	21 $\bar{5}$	<i>w.</i>
			{116		{116}	1.437	0.6322	0.6320	020
1.397	0.6682	{0.6685	{116}	<i>v.w.</i>	(1.428	0.6402	0.6400	020	<i>w.)</i>
		{0.6699	70 $\bar{1}$ }		1.409	0.6581	0.6593	70 $\bar{1}$	
1.374	0.6916	{0.6707	505}	<i>v.w.</i>	1.369	0.6977	0.6976	514	<i>w.</i>
		{0.6915	022}		{0.6928	604}			

v.w. = very weak, *w.* = weak, *m.* = moderately strong, *st.* = strong, *v.st.* = very strong, *br.* = broadened.

2(b). This specimen is also remarkable, because of the fact that no water is present. As the analysis was carried out in a tent, it seems that the values are not quite reliable, and a new analysis is desirable.

Gruner also gives other reasons why the O of the water differs structurally from the other oxygen ions in the compound. None of his reasons, however, is in contradiction to the formula suggested by us. The fact that practically all the water can be driven off without collapse of the structure indicates that at the same time part of the bivalent (or trivalent) Mn ions are oxidized to tetravalent Mn, and thus the number of anions in the unit cell is maintained. For some of the specimens listed in Tables 2 and 3, the Mn^{2+} content is lower than this explanation would imply (cryptomelane 1 in Table 2 and cryptomelane 3 and 4 in Table 3). It is, however, just those specimens where the adsorption probably is great. A study of the change of cell dimensions and densities after driving off the water would be desirable, and if we can obtain material for such an investigation it will be made.

However, if Gruner's assumption that the water is of zeolitic nature is correct, the water should be regained as easily as it is driven off, and all or practically all of it should be reabsorbed, which is not the case, as is evident from Gruner's own experiment. The behaviour of the specimen from Romanèche is just what would be expected if our explanation is valid.

8. α - MnO_2

Evidently from the isostructural relationship between α - MnO_2 and hollandite, it follows that α - MnO_2 must hold some large ions, as, for example, K^+ , to prevent the structure from collapsing. The necessity of K^+ ions for the formation of α - MnO_2 has been pointed out by Cole *et al.* (1947).

Gruner's experiment on the cation exchange of α - MnO_2 shows that Ag^+ ions enter the structure more readily than the larger Pb^{2+} and Ba^{2+} ions. This is evidently what is to be expected from the structure, as the short A - A distances of about 2.8 Å. must lead to a certain instability of the structure, because of strong repulsive forces between the cations, and these forces must apparently be less for the smaller ions. In accordance with this the twofold position can be filled to a larger extent with a larger number of adjacent A ions, when these ions are smaller and of less valency, i.e. as is the case for Ag^+ compared with Pb^{2+} and Ba^{2+} .

9. A comparison of the structures of α - MnO_2 , β - MnO_2 , γ - MnO_2 and ramsdellite

As will be seen from Fig. 3, the network of oxygen octahedra is principally the same in β - MnO_2 (pyrolusite) and ramsdellite. In β - MnO_2 every other octahedron is occupied by a Mn ion both in the a and b directions. However, in ramsdellite there are pairs of occupied and unoccupied octahedra in the b direction, but in the a

direction every other octahedron is filled. Obviously, in α - MnO_2 the a and b directions of pyrolusite and ramsdellite corresponds to $[110]$ and $[1\bar{1}0]$ (Fig. 2). Some of the oxygen atoms in the network are substituted with K^+ ions, but if octahedron chains are considered, in which the K^+ ions do not take part, we find in both the $[110]$ and $[1\bar{1}0]$ directions pairs of occupied and unoccupied octahedra, as in the b direction in ramsdellite.

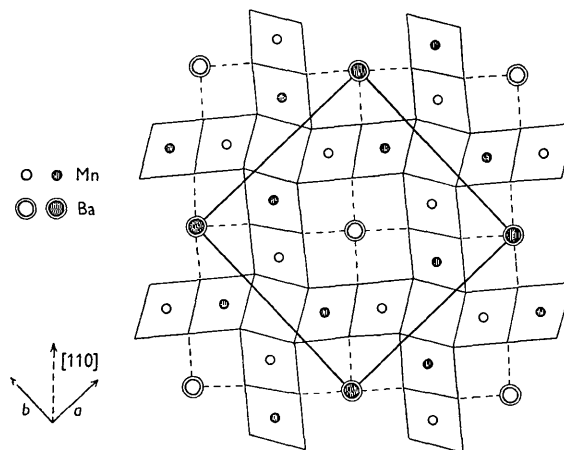


Fig. 2. The network of oxygen octahedra in hollandite projected on (001).

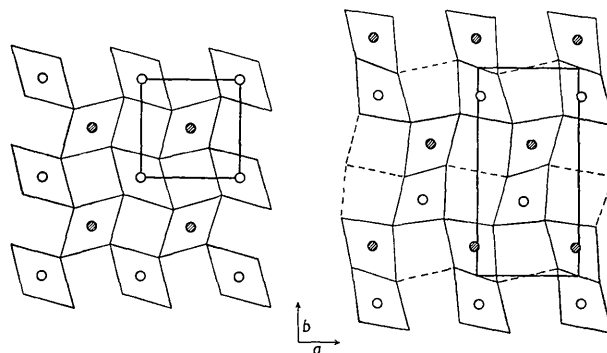


Fig. 3. The network of oxygen octahedra in pyrolusite (to the left) and ramsdellite (to the right) projected on (001). The circles denote Mn ions.

There is also a close similarity in the corresponding spacings. Along $[110]$ in α - MnO_2 we find six octahedra and along $[010]$ in ramsdellite four. The length of $[110]$ is $\sqrt{2} \times 9.8$ Å., and recalculated on four octahedra this corresponds to $\frac{4}{6} \sqrt{2} \times 9.8 = 9.2$ Å., to be compared with 9.27 Å. for the b axis in ramsdellite.

The structure of γ - MnO_2 has not been definitely established (Cole *et al.* 1947; Byström, 1949), but it seems that the structure is partly disordered, and possibly the arrangement of the Mn ions changes from ramsdellite to pyrolusite at random.* The cell dimen-

* In a recent paper McMurdie (1948) concludes from powder photographs that γ - MnO_2 must have a disordered pyrolusite structure. However, from the spacings it is obvious that the substance which he has called γ - MnO_2 is not identical with the oxide called γ - MnO_2 by Cole *et al.* (1947) and by Byström (1949), but is rather a poor β - MnO_2 preparation.

Table 5. Comparison between observed and calculated F values in hollandite F values from Weissenberg photographs of hollandite 1, taken with Cr K radiation.

hkl	$ F _{\text{obs.}}$	$F_{\text{Met.}}$	$F_{\text{Oxy.}}$	$\Sigma F_{\text{calc.}}$	hkl	$ F _{\text{obs.}}$	$F_{\text{Met.}}$	$F_{\text{Oxy.}}$	$\Sigma F_{\text{calc.}}$
110	18	-11	-17	-28	170	52	-31	-15	-46
220	58	65	-12	53	820	11	31	-10	21
330	35	-100	70	-30	280	36	27	10	37
440	90	75	-4	71	101	25	-41	7	-34
550	33	23	-2	21	301	82	-35	-73	-108
660	100	106	20	126	501	24	-7	18	11
200	39	-31	-20	-51	701	34	-46	21	-25
400	64	-53	-23	-76	211	60	79	-10	69
600	150	138	44	182	121	54	-87	28	-59
800	10	10	-24	-14	411	98	-114	-8	-122
310	85	99	-5	94	141	53	39	19	58
130	100	132	-13	119	611	58	-58	2	-56
420	64	87	-36	51	161	≤ 20	-10	-2	-12
240	94	53	31	84	321	≤ 20	-9	12	3
530	32	50	-13	37	231	37	-27	5	-22
350	75	77	-20	57	521	88	57	17	74
640	16	-11	-4	-15	251	125	-129	-6	-135
460	81	-56	-5	-61	721	38	-69	23	-46
510	66	21	26	47	271	38	55	-30	25
150	32	2	-30	-28	431	≤ 20	-26	15	-11
620	40	-37	0	-37	341	≤ 20	-1	9	8
260	≤ 20	11	-13	-2	631	37	-22	-33	-55
730	108	107	-23	84	361	37	-22	-33	-55
370	90	85	-16	69	541	150	-118	-34	-152
710	≤ 20	6	14	20	451	80	28	27	55

sions of γ - MnO_2 indicate that the ramsdellite arrangement dominates. Attempts will be made to calculate the percentage of each arrangement from the intensity and broadening of the reflexions.

A large number of syntheses shows that by the precipitation of manganese dioxide, either α - MnO_2 or γ - MnO_2 is obtained. A possible explanation is that the primary product by these precipitations is the double strings, which are common for the α - MnO_2 and ramsdellite structures. If large ions are present, the double strings cluster together around these in the α - MnO_2 manner. These precipitates, after annealing at low temperature or after hydrothermal treatment, show the reflexions of an undeformed hollandite structure. If no large ions are present (or if the concentration is too low), the double strings are knitted together to a ramsdellite-like arrangement. However, by the annealing of these precipitates by boiling with water, there is a tendency for the Mn ions to change positions to those of pyrolusite, and thus a partly disordered structure results. If the annealing temperature is high (300° C.), a complete transformation to pyrolusite occurs.

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