

## The Symmetry and Crystal Structure of Manganite, $Mn(OH)O$ .

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### Abstract.

A rough structure for manganite has already been proposed by Garrido. Although unrecognized, this is a marcasite-like structure. From its formula, manganite ought rather to have an arsenopyrite-like structure, which is a superstructure based upon the marcasite type. A new structural investigation shows that this is the case.

Manganite is definitely monoclinic, not orthorhombic, as stated in all reference books. This lowered symmetry is evidenced by the polysynthetic twinning on the supposed symmetry plane, (100), by inclined extinction in systems of twin bands in cleavage flakes, and by the diffraction symmetry,  $2/m$ .

The new structural investigation has been made by the equi-inclination Weissenberg method and inspective interpretation of films. The manganite structure has the following characteristics (customary manganite orientation):

Space group:	$B2_1/d$	Equipoints: all atoms in general position.
Unit cell:	$a = 8.86 \text{ \AA}$	Parameters: $x_a$ $y_b$ $z_c$
	$b = 5.24$	$Mn \sim 0$ $\sim 0$ .258
	$c = 5.70$	$O_1$ .119   .122   0
	$\beta = 90^\circ$	$O_2$ .119   .122   .500

The formula  $Mn(OH)O$  corresponds geometrically and physically with the arsenopyrite formula  $FeAsS$ ; the  $O_1$  atoms are almost certainly  $(OH)$  groups having a function similar to  $As$  and  $Sb$  in arsenopyrite and gudmundite. The  $(OH)$  group has a radius about .07  $\text{\AA}$  greater than the  $O$  atom.

The structure, although resembling the arsenopyrite structure, is, in greater detail, a layer structure:  $Mn$  is in square coordination between  $2(OH)$  and  $2O$  in the same (010) sheet with one more  $(OH)$  and one more  $O$  above and below the center of the square and in adjacent sheets in such a way as to approach octahedral coordination for the  $Mn$ . The hydrogen bonding and the mild layering of the structure into (010) sheets account perfectly for the outstanding (010) cleavage and the (010) translation-gliding plane.

### Introduction.

A crystal structure of manganite has recently been proposed by Garrido<sup>1)</sup>. Although recognizing that certain faint reflections required doubling of his cell axes in two directions, Garrido derived a rough structure with the following characteristics:

$$a = 4.42 \text{ \AA} \qquad b = 5.23 \text{ \AA} \qquad c = 2.87 \text{ \AA}.$$

1) Garrido, M. J., Structure de la manganite, Bull. Soc. Franç. Minéral. **58** (1935) 224—244.

Formula weights per cell =  $2MnO(OH)$

Space group:  $V_h^{12}$

$Mn$  at  $000$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

$O$  at  $uv0$ ;  $\bar{u}\bar{v}0$ ;  $\frac{1}{2}-u, \frac{1}{2}+v, \frac{1}{2}$ ;  $\frac{1}{2}+u, \frac{1}{2}-v, \frac{1}{2}$ .

where  $u = .25$

$v = .338$

Although Garrido apparently did not recognize the fact, this is a marcasite-type structure, a correlation which becomes apparent if manganite is referred to the marcasite orientation. This is done by means of the following cyclical permutation of axes:

manganite	→	marcasite
$a$	→	$b$
$b$	→	$c$
$c$	→	$a$

Garrido's manganite and the marcasite minerals then compare as follows, using the marcasite orientation:

	manganite	marcasite	löllingite
$a$	2.87	3.37	2.85
$b$	4.42	4.44	5.25
$c$	5.23	5.39	5.92

Formula weights

per cell:

$2Mn(OH)O$        $2FeSS$        $2FeAsAs$

Space group:

$Pmn\bar{n} - V_h^{12}$

Metal position:

$000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$

Non-metal position:

$0uv; 0\bar{u}\bar{v}; \frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}+v; \frac{1}{2}, \frac{1}{2}+u, \frac{1}{2}-v.$

Non-metal parameters:  $u$

.25

.203

.175

$v$

.338

.375

.361

From this point on, the standard manganite orientation will be employed in discussing manganite.

Now, the formula type of manganite,  $Mn(OH)O$ , is not the  $AB_2$  type required for the customary marcasite structure. It corresponds, rather, with the arsenopyrite type of formula,  $AB'B'$ , and therefore manganite should be investigated for arsenopyrite-like characteristics. These have been listed in the arsenopyrite paper<sup>1)</sup>, to which tabulation the following references apply.

Garrido has already presented a certain amount of evidence tending to corroborate a conjecture that manganite has the arsenopyrite type crystal structure. Thus, he found faint reflections indicating that the true cell should have double the  $a$  and  $c$  axes of the one he chose for the rough structure. This confirms characteristic 4. (See tabulation in the arsenopyrite paper.) A preliminary investigation by the writer developed the fact that the 0.0.4 series of spectra constitutes a gradually declining<sup>2)</sup> intensity series rather than a regularly declining series which characterizes the pure marcasite type of structure. Manganite therefore has certain arsenopyrite-like characteristics.

1) Buerger, M. J., The symmetry and crystal structure of the minerals of the arsenopyrite group. *Z. Kristallogr. (A)* **95** (1936) 112—113.

2) Buerger, M. J., op. cit., 91—92.

**Notes on the Symmetry of Manganite.**

The writer had access to a number of manganite specimens from Ilfeld, Germany, which is also the locality of Garrido's material. A number of analyses of manganite from this locality have been collected by Koechlin<sup>1</sup>).

In the best of this material, from which small crystals were selected for X-ray investigation, it is quite apparent that there are twin lamellae parallel to (100) which show up plainly on the crystal terminations. Since (100) would be a symmetry plane if manganite were orthorhombic, and since twinning cannot occur on a symmetry plane, it is clear that manganite cannot be orthorhombic, as recorded in all reference books. The symmetry of manganite has been under suspicion before, but the anomalies have always been explained away. The subject is reviewed by Koechlin<sup>2</sup>) and by Hintze<sup>3</sup>).

Important evidence for a symmetry lower than orthorhombic is the inclined extinction of alternate systems of bands<sup>4</sup>)<sup>5</sup>) seen by transmitted polarized light in thin cleavage flakes. These bands are evidently the cross-sections of the (100) twin lamellae mentioned above.

To these evidences of lower symmetry, the writer adds the following: If a manganite cleavage splinter (bounded by the excellent (010) and perfect (110) cleavages) is set up on a two-circle goniometer with the cleavage zone taken as the equator, then the natural (001) surface may have a  $\rho$  coordinate of almost  $4^\circ$ . This should be  $0^\circ$  if the crystal is orthorhombic, and it is this deviation which permits the polysynthetic twinning to be observed on the basal termination of the crystal. This face, however, is a vicinal one and not the structural pinacoid, for crystal settings made with its use give poorly oriented X-ray photographs.

1) Koechlin, R., in Doelter, C. and Leitmeier, H., *Handbuch der Mineralchemie*, III<sub>2</sub>, 1926, pp. 847—848, analyses 4, 5, 6, 10, 13, 14, 15, 16, 17.

2) Koechlin, R., *op. cit.*, p. 847.

3) Hintze, Carl, *Handbuch der Mineralogie*, vol. 1, part 2, 1915, p. 1978, especially footnote 1.

4) Mügge, O., Zur Kenntnis der optischen und Kohäsionseigenschaften des Manganit. *Zbl. Mineral., Geol., Paläont.* **1922**, 1—2.

5) Garrido, M. J., Structure de la manganite, *Bull. Soc. Franç. Minéral.* **58** (1935) 225.

### Method.

The X-ray study has been carried on entirely by the equi-inclination Weissenberg method<sup>(1)(2)(3)</sup> and all films have been interpreted by the inspective method without indexing procedure. The cell characteristics were derived from films made with  $F\alpha K$  radiation. The parameters were fixed from reflection intensities recorded on two complete sets of equatorial films, one set under-exposed to differentiate the intensities of the strong reflections and the other set over-exposed to allow comparisons between weak reflections.

### Cell Characteristics.

Diffraction symmetry. — The equi-inclination Weissenberg photographs for rotations about each of the three customary manganite axes all display a position symmetry which cannot be distinguished from  $C_{2l}$ . The intensity distributions, however, are partly of lower symmetry:

Rotations about the  $b$  axis give equi-inclination Weissenberg films displaying the symmetry  $C_2$  for all levels. Rotations about the customary manganite  $a$  and  $c$  axes both display the symmetry  $C_{2l}$  for the zero levels and  $C_l$  for the  $n$ -levels. (See Figs. 1–5).

Fig. 1–5. Proof of the inferior symmetry of manganite and of the  $B$ -centered nature of the manganite lattice referred to the customary manganite axial orientation. Note that all photographs display the position symmetry  $C_{2l}$ , with the symmetry lines in the positions indicated by both full and broken inked lines. The intensity distributions, however, display a lower symmetry in some cases: only the full lines are true symmetry lines when account is taken of the intensity distribution. The photographs indicate the following information:

	symmetry	corresponding orthorhombic plane lattice pattern	corresponding orthorhombic stacking sequence
Fig. 1: $a$ axis equator	$C_{2l}$	11	} 10
Fig. 2: $a$ axis 1st layer	$C_l$	10	
Fig. 3: $c$ axis equator	$C_{2l}$	11	} 10
Fig. 4: $c$ axis 1st layer	$C_l$	10	
Fig. 5: $b$ axis equator	$C_2$	8	7

This information constitutes proof that the cell is  $B$ -centered with the customary manganite axial orientation and that manganite is monoclinic with the  $b$  axis as the 2-fold axis.

1) Buerger, M. J., The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs: *Z. Kristallogr. (A)* **88** (1934) 356–380.

2) Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Z. Kristallogr. (A)* **91** (1935) 255–289.

3) Buerger, M. J., An apparatus for conveniently taking equi-inclination Weissenberg photographs: *Z. Kristallogr. (A)* **94** (1936) 87–99.

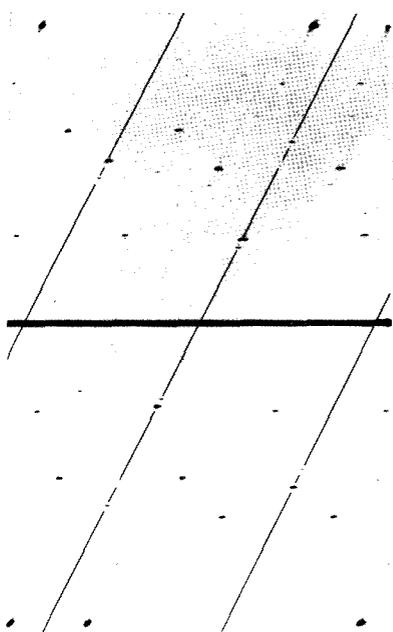


Fig. 1.

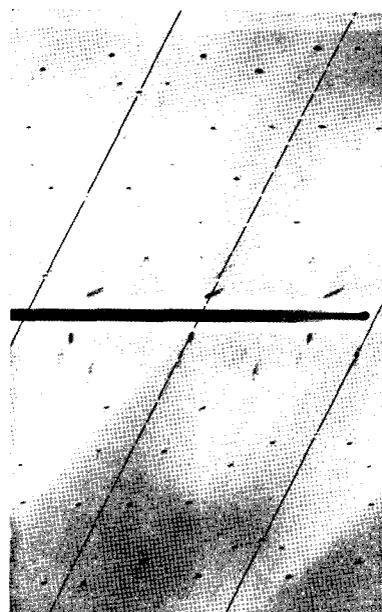


Fig. 2.



Fig. 3.

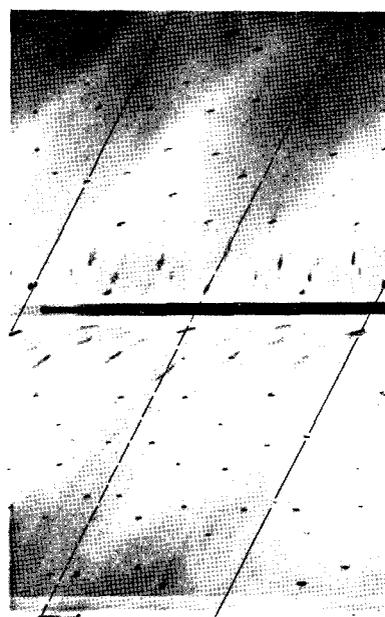


Fig. 4.

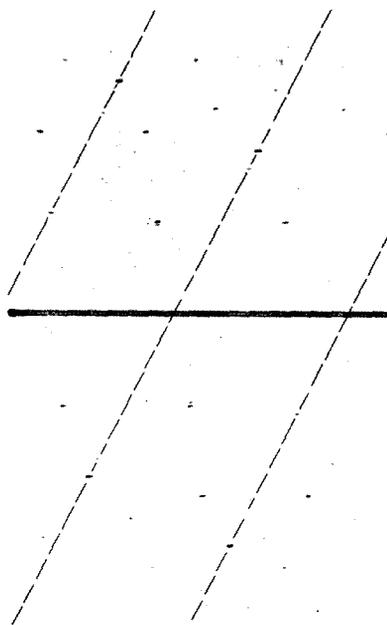


Fig. 5.

axes. The customary manganite axes may be retained, however, by choosing a doubly primitive, *B*-centered cell. This alternative choice is desirable for it brings out the pseudo-orthorhombic character of the crystal and also avoids the confusion of a new orientation.

The *B*-centering of the manganite cell may now be justified in some detail, because this is contrary to Garrido's indexing. A rigorous study of the *B*-centering was made by comparison of the several equi-inclination photographs for the same axial rotation. All levels for rotation about the *b* axis display the plane lattice type<sup>1</sup>) 8 (referring in this discussion to the corresponding orthorhombic level patterns because of the strong pseudo-orthorhombic dimensional aspect). For rotations about the *a* and *c* axes, the level patterns are type 11 for even levels and type 10 for odd levels, (Figs. 1–5) i. e., the plane net stacks are both of type 10. The lattice is therefore *B*-centered with the axes chosen.

Cell dimensions. — A study of the rotations about the three conventional manganite axes, together with a study of several Weissenberg photographs indicates the following cell:

1) Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Z. Kristallogr. (A)* **91** (1935) 255–289.

The diffraction symmetry is thus plainly  $2/m$ , and the crystal system is plainly monoclinic, in harmony with the symmetry observations already made. The customary manganite *b* axis is the two-fold axis; no change in the customary manganite orientation need therefore be made from a point of view of symmetry.

Space lattice type. — The patterns of the equi-inclination photographs of the various levels for the *b* axis rotation are all identical, indicating that the primitive and not the centered monoclinic lattice is the basic group of translations for manganite. The *a* and *c* axes of this primitive translation unit extend in the  $[101]$  and  $[\bar{1}01]$  directions referred to an appropriate cell with edges parallel to the customary manganite

	Garrido	Buerger
$a$	8.84 Å	8.86 Å
$b$	5.23	5.24
$c$	5.74	5.70

Garrido's values for the larger unit are also given in comparison. The two sets of values are in good agreement. This cell accommodates 8 formula weights of  $Mn(OH)O$ .

Space group. — A comparison of equatorial films with the  $n$ -layer equi-inclination films reveals the characteristic extinctions of space group  $B2_1/d$  discussed in detail in the arsenopyrite paper<sup>1</sup>).

### The Crystal Structure.

General argument. — It should be pointed out that from the cell dimensions, end-centering, and pinacoid reflection intensity series it can be proven that manganite cannot be referred to an orthorhombic space group, even without the several symmetry evidences already given. This elimination of orthorhombic space groups follows the discussion given in the arsenopyrite paper.

Since the space group extinctions can be recognized, it is possible to seek appropriate parameters in the correct space group  $B2_1/d$  directly. In the initial stages of this investigation, however, crystals sufficiently free from twinning were not utilized to enable the space group to be recognized easily by its extinctions, so that indirect approaches were of considerable assistance, and even now, they add confidence in the correctness of the final structure.

An indirect approach to the structure may be made with the aid of Garrido's rough structure: If no distinction is made between  $(OH)$  and  $O$ , then manganite has a rough marcasite structure. If account is now taken of the true cell characteristics and also of the alternation of  $(OH)$  and  $O$ , then it can be shown<sup>2</sup>) that there are only five possible types of alternations, belonging variously to space groups  $Cm$ ,  $C2$ , and  $B2_1/d$ . Only the last space group gives the extinctions actually observed in manganite. To this space group belong two related types of alternations, designated  $ab'ba'$  and  $cd'dc'$ , differing only in the position of the manganese atom. Instead of blindly seeking parameters in space group  $B2_1/d$ ,

1) Buerger, M. J., The symmetry and crystal structure of the minerals of the arsenopyrite group. *Z. Kristallogr. (A)* **95** (1936) 83.

2) Buerger, M. J., A systematic method of investigating superstructures, applied to the arsenopyrite crystal structural type. *Z. Kristallogr. (A)* **94** (1936) 425.

it is desirable to examine the parameters in the regions of the two possible structures  $ab'ba'$  and  $cd'dc'$ , which considerably shortens the labor of selecting the correct structure.

Structure  $ab'ba'$ . — In this structure, the  $Mn$  atoms occupy symmetry centers and hence are without degrees of freedom. By trial variations of the parameters of the remaining atoms—two varieties of oxygen—it can be shown that the  $h00$ ,  $00l$  and  $h0h$  reflection intensities cannot be simultaneously satisfied. This structure is also physically unlikely as pointed out in the arsenopyrite paper.

Structure  $cd'dc'$ . — This alternative possibility is undoubtedly the correct structure. It gives an excellent explanation of the intensities with appropriate parameters. Unfortunately, with the identical scattering powers of  $(OH)$  and  $O$  (as compared with the corresponding  $As$  and  $S$  in arsenopyrite) it is difficult to place these units separately. An approximation is possible, however, based upon the parameter combinations found in the other arsenopyrite-like minerals. It is found that the nearer the non-metals are in radius, the more nearly identical are corresponding parameters for the two non-metals. With this approximation the parameters for the  $ab$  projection may be found.

In the case of the manganite from which the writer's films were prepared, an attempt was made to secure material free from twinning. While a measure of success was achieved in eliminating twinned areas, a truly perfect single crystal was not obtained. This makes the comparison of odd with even orders of 101 somewhat unreliable.

The parameters for manganite are as follows:

	$\Theta_a$	$\Theta_b$	$\Theta_c$	$x_a$	$y_b$	$z_c$
$Mn$	$\sim 0^\circ$	$\sim 0^\circ$	$93^\circ$	$\sim .000$	$\sim .000$	.258
$O_1$	$43^\circ$	$44^\circ$	$0^\circ$	.119	.122	.000
$O_2$	$43^\circ$	$44^\circ$	$180^\circ$	.119	.122	.500

A comparison of observed intensities with those calculated for these parameters is given in table I.

Table I. Comparison of calculated and observed reflection intensities for manganite.

orders of 100		orders of 101		orders of 001		orders of 010	
calculated	observed	calculated	observed	calculated	observed	calculated	observed
8 = 369	8	2 = 918	2			8 = 369	8
	∇						∇
4 = 168	4	6 = 78	∇	gradual	gradual	4 = 168	4
24 = 54	∇	4 = 72	4, 6, 8	decline	decline	24 = 54	∇
	16, 24						16, 24
16 = 43	∇	8 = 51	∇			16 = 43	∇
12 = 25	12	13 = 41.3	13			12 = 25	12
	∇						∇
20 = 7	20	3 = 11.2	3			20 = 7	20
			∇				
		5 = 8.7	5				
			∇				
		10 = 8.2	7				
			∇				
		7 = 5.8	∇				
		11 = 4.8	10, 9, 11				
		9 = 4.4	∇				
		12 = 2.4	12				

**Discussion of the Structure.**

The manganite structure is shown in figure 6. Certain of its interatomic distances calculated on the assumption of orthogonal axes are given in table II.

Table II. Interatomic distances between nearest neighbors in manganite.

atom	coordinates	neighbor	coordinates	distance
$Mn$	$xyz$	$O_1$	$-x + \frac{1}{4}, y - \frac{1}{2}, -z + \frac{1}{4}$	$\sim 2.30 \text{ \AA}$
		$O_1$	$x, y, z$	1.92
		$O_1$	$-x, -y, -z$	
		$O_2$	$x - \frac{1}{4}, -y + \frac{1}{2}, z - \frac{1}{4}$	
		$O_2$	$x, y, z$	1.85
		$O_2$	$-x, -y, -z + 1$	
		$Mn$	$-x, -y, -z + 1$	
		$Mn$	$-x, -y, -z$	2.94

Table II (continuation).

atom	coordinates	neighbor	coordinates	distance
$O_1$	$xyz$	$Mn$	$-x + \frac{1}{4}, y + \frac{1}{2}, -z + \frac{1}{4}$	$\sim 2.30$
		$Mn$	$x, y, z$	} 1.92
		$Mn$	$-x, -y, -z$	
		$O_2$	$-x + \frac{1}{2}, -y, -z + \frac{1}{2}$	
		$O_2$	$x, y, z$	} 2.85
		$O_2$	$x, y, z - 1$	
		$O_2$	$x - \frac{1}{4}, -y + \frac{1}{2}, z - \frac{1}{4}$	
		$O_1$	$-x, -y, -z$	2.47
		$O_1$	$x + \frac{1}{4}, -y + \frac{1}{2}, z + \frac{1}{4}$	2.96
$O_1$	$-x + \frac{1}{4}, y + \frac{1}{2}, -z + \frac{1}{4}$	2.99		
$O_2$	$xyz$	$Mn$	$x + \frac{1}{4}, -y + \frac{1}{2}, z + \frac{1}{4}$	$\sim 2.30$
		$Mn$	$x, y, z$	} 1.85
		$Mn$	$-x, -y, -z + 1$	
		$O_1$	$-x + \frac{1}{2}, -y, -z + \frac{1}{2}$	
		$O_1$	$x, y, z$	} 2.85
		$O_1$	$x, y, z + 1$	
		$O_1$	$-x + \frac{1}{4}, y - \frac{1}{2}, -z + \frac{1}{4}$	
		$O_2$	$-x, -y, -z + 1$	2.47
		$O_2$	$x + \frac{1}{4}, -y + \frac{1}{2}, z + \frac{1}{4}$	2.96
		$O_2$	$-x + \frac{1}{4}, y + \frac{1}{2}, -z + \frac{1}{4}$	2.99

The structure presents some interesting features. To the first approximation, it may be said that the structure is rutile-like. The manganese atoms occupy the centers of oxygen octahedra which form strings along the  $c$  axis by sharing edges. The strong cation-anion bonds within these units account for the several cleavages in the prismatic zone. The relative perfection of these various cleavages is considerably modified by the additional bonding and the layering indicated beyond.

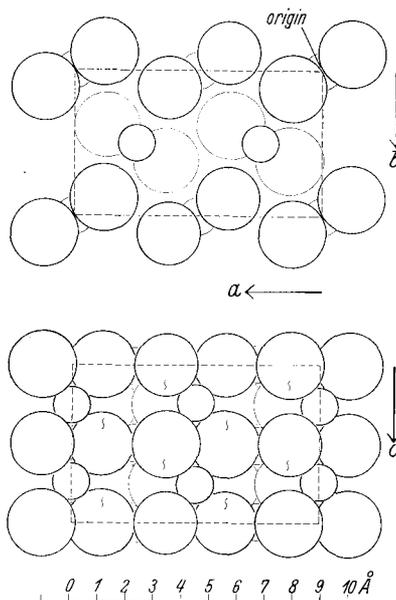
There are four kinds of  $Mn-O$  distances:

in the plane of the shared edges	{	two of 1.85 Å
	}	two of 1.92 Å
outside the plane of the shared edges	{	one of $\sim 2.30$ Å
	}	one of 2.30 Å

The first four distances can be rather accurately determined, the last two cannot. It is rather certain, however, that the manganese is closer to a coordination square of oxygen atoms than to the other two oxygen atoms. The greater distances of the last two oxygen atoms make the structure approach a layer structure type.

The  $O-O$  distance along the shared edges is  $2.47 \text{ \AA}$  which is the same as is found in rutile. The  $O-O$  distance between the oxygens belonging to different unshared cation coordinations, however, is subnormal, namely  $2.65 \text{ \AA}$ . This evidently indicates a hydrogen bond of some sort, but apparently not the hydrogen bond as ordinarily understood. If an ordinary hydrogen bond were in this position, with the hydrogen located equally between the two neighboring oxygens, then all oxygen-manganese distances would be the same and the crystal would

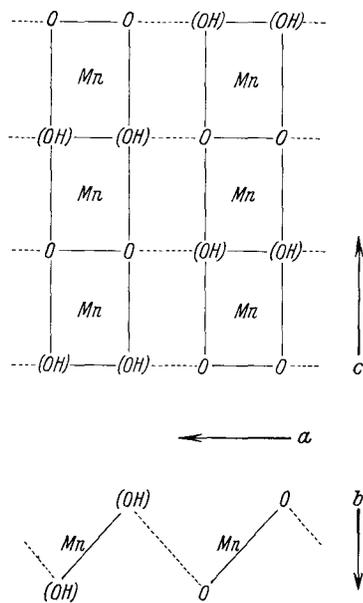
Fig. 6.  
 The crystal structure of manganite as seen along the  $c$  axis (upper diagram) and along the  $b$  axis (lower diagram). The locations of the screw axes are shown. Diamond glide planes (glide-components  $a/4 + c/4$ ) occur at  $\frac{1}{4}$  and  $\frac{3}{4}$  normal to  $b$  but are omitted for sake of clearness. Inversion centers occur between the oxygen pairs. Small atoms are manganese, large atoms oxygen. The latter are of two slightly different sizes, the larger of which (showing no gaps between pairs) are probably essentially hydroxyl groups.



have degenerate  $a$  and  $c$  identity periods, i. e., manganite would be a marcasite-like, not an arsenopyrite-like crystal. The only way of accounting for these doubled marcasite axes in manganite is either by assuming something different about two of the four  $Mn-O$  bonds in the plane of the shared edges to account for the two different  $Mn-O$  distances there, or by assuming that  $O_1$  and  $O_2$  have different characters, including radii, as in the case of the other arsenopyrite group crystals. With the latter assumption, manganite gives a good parallel with arsenopyrite group crystals if  $O_1$  is regarded as  $(OH)$  and compared with  $As$  in arsenopyrite, while  $O_2$  is regarded as oxygen and compared with  $S$  in arsenopyrite. Adopting the designation  $(OH)$  for  $O_1$  and  $O$  for  $O_2$ , it becomes apparent that the  $Mn-(OH)$  distance and the  $Mn-O$  distance in the plane of

the shared edge give the  $(OH)$  group a radius greater than the oxygen atom radius by about  $.07 \text{ \AA}$ .

The bonding may now be examined in somewhat greater detail. The manganese atoms are more accurately described as located at the centers of oxygen-hydroxyl squares which join edges to form tilted ribbons running down the  $c$  axis, thus:



The  $(OH)$  groups of one ribbon, bond themselves to the  $O$  atoms of the adjacent ribbons to form a  $(010)$  sheet corrugated in the direction  $[001]$ . The additional  $(OH)-O$  bonds within the  $(010)$  sheets make them strong structural units. The outstanding excellence of the  $(010)$  cleavage over the other cleavages in the prismatic zone is thus produced. Since the sheets are corrugated along  $[001]$  and have an appropriate charge distribution<sup>1)</sup> the structure also accounts perfectly for the gliding elements  $T = (010)$ ,  $t = [001]$ , discovered by Mügge<sup>2)</sup>.

The somewhat greater  $Mn-O$  and  $Mn-(OH)$  distance between these  $(010)$  sheets than within them has a tendency to make the structure a mild layer structure. This feature enhances the ease of cleavage and gliding.

1) Buerger, M. J., Translation-gliding in crystals of the  $NaCl$  structural type. *Amer. Mineralogist* **15** (1930) 237.

2) Mügge, O., Zur Kenntnis der optischen und Kohäsionseigenschaften des Manganit. *Zbl. Mineral., Geol., Paläont.* **1922**, pp. 1—2.

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Received 11. July 1936.