

The Crystal Structure of Ramsdellite, an Orthorhombic Modification of MnO_2

ANN MARIE BYSTRÖM

Geological Survey of Sweden, Stockholm 50, and Institute of Physical and Inorganic Chemistry, University of Stockholm, Stockholm, Sweden

In the course of an investigation of the hollandite minerals from the Ultevis district¹ attempts were made to synthesize products isomorphous with these minerals. In connection with this work there appeared a phase that was found to be a modification of MnO_2 , previously described by Glemser² as $\gamma\text{-MnO}_2$. It was considered of great interest to investigate the structure of this simple manganese dioxide before any further investigation was made of the more complicated manganese oxide minerals. Since the substances obtained before had given rather diffuse X-ray patterns, and as it was desirable to have crystals large enough for single crystal investigation, the syntheses were directed with a view to giving macrocrystals. $\gamma\text{-MnO}_2$ was prepared in ways 1) and 2) described by Glemser² and the preparations obtained were then treated in the following ways.

a) Hydrothermally at various temperatures; the preparations were placed in a platinum crucible, enclosed in a steel bomb. The products obtained all gave the X-ray patterns of pyrolusite.

b) The preparations were heated in sealed glass tubes with nitric acid and sulphuric acid of various concentrations, at temperatures from 120° C to 170° C. When sulphuric acid was used the products gave X-ray patterns of $\gamma\text{-MnO}_2$, somewhat sharpened compared with the initial ones. With nitric acid pyrolusite was obtained except in one case where a new phase appeared, which, however, gave only two reflections in the powder pattern. Neither of these reflections belonged to pyrolusite or $\gamma\text{-MnO}_2$.

In no case was there any sign of macroscopical crystals and in order to get products giving sharp powder patterns at least, the preparations were boiled for several days with either nitric or sulphuric acid with the use of

reflux. They were also heated for various lengths of time up to 200° C, but the experiments were not very successful.

In 1947 Cole, Wadsley and Walkley³ published a study on manganese dioxide. They had synthesized preparations of γ -MnO₂, giving good X-ray powder patterns. By comparison they found that in intensities and spacings these agreed closely with the powder patterns of ramsdellite as given by Fleischer and Richmond⁴. In a collection of manganese oxide minerals, which Mr. Fleischer had kindly placed at the disposal of the Geological Survey of Sweden for identification of the Swedish manganese oxide minerals, there was a sample of ramsdellite from Lake Valley, New Mexico. As this mineral was exactly what I had tried to prepare, I took the liberty to use it for further investigations.

The mineral consisted of aggregates of small subparallel needle crystals, which gave it a platy appearance, as first described by Ramsdell⁵. It fell easily to pieces and it was difficult to find a crystal to mount on a goniometer. The needles were too small to be handled by themselves, but a fragment of parallel needles could be used to give Weissenberg photographs. That the fragment used was not composed of absolutely parallel needle crystals, was probably the reason why a few discrepancies appeared in the intensities of the Weissenberg photographs, as will be seen later. Rotation and Weissenberg photographs were made, rotating the crystal around two axes at right angles. The symmetry was found to be orthorhombic, as had already been stated by Fleischer and Richmond⁴, and preliminary cell dimensions were determined. * These were later used to index the powder photographs, from which more accurate values were obtained. The powder photographs were taken with focusing cameras with both Fe-K and Cr-K radiation. They gave the cell dimensions $a = 4.533 \pm 0.005 \text{ \AA}$, $b = 9.27 \pm 0.01 \text{ \AA}$ and $c = 2.866 \pm 0.005 \text{ \AA}$, ($a = 4.524 \text{ kX}$, $b = 9.25 \text{ kX}$ and $c = 2.860 \text{ kX}$), which as we see, hold a simple relation to those of pyrolusite ($a = 4.40 \text{ \AA}$, $c = 2.87 \text{ \AA}$): the c -axis is of the same length, the a -axis is slightly longer and the b -axis a little more than double. Consequently, the cell volume of ramsdellite is practically twice that of pyrolusite, and as there are two formula units of MnO₂ in the tetragonal cell, there ought to be four in the orthorhombic cell. Then the calculated specific gravity is 4.84 and in good agreement with the observed value 4.83. Like most pyrolusites occurring in nature, ramsdellite, too, contains water and various other oxides. The foreign elements amount to nearly 5% in the

* Mr Richmond had also made an approximate determination of the unit cell, $a = 4.5 \text{ \AA}$, $b = 9.2 \text{ \AA}$ and $c = 2.83 \text{ \AA}$, which was privately communicated to me, when this work was already completed.

examined mineral — ($\text{SiO}_2 - 0.8\%$, $\text{TiO}_2 - 0.2\%$, $\text{Al}_2\text{O}_3 - 0.8\%$, $\text{Fe}_2\text{O}_3 - 1.2\%$, $\text{CaO} - 0.2\%$ and $\text{H}_2\text{O} - 1.3\%$). It cannot be decided if the mineral contains these substances merely as impurities, or if the manganese atoms are partly replaced by some of the other metal atoms. In any case, the structure factors would not differ appreciably and in the following calculations the mineral is treated as pure MnO_2 .

The Weissenberg photographs obtained registered the reflections $hk0$, $hk1$, $0kl$ and $1kl$. There are no systematic extinctions for the reflections hkl or $hk0$, but those of the type $h0l$ are only present for $h+l = 2n$, and those of the type $0kl$ for $k = 2n$. This is characteristic for space groups D_{2h}^{16} and C_{2v}^9 . For the positions of the atoms the space group $D_{2h}^{16} - \text{Pbnm}$ will be considered, the axes being changed as compared with the diagram in the *International tables* (1935). The relation between the axes is $a'b'c' = cab$, where $a'b'c'$ are the axes here chosen. There are four manganese atoms and eight oxygen atoms to place, and preliminary calculations show that the two sets of fourfold positions without parameters are altogether out of the question. If the four metal atoms are placed in 4 : (c) $xy\frac{1}{4}$; $xy\frac{3}{4}$; $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{3}{4}$; $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{4}$, there is an agreement between the values observed and calculated for the parameters $2\pi x = 10^\circ$ and $2\pi y = 50^\circ$. On account of lack of space the eight oxygen atoms cannot be placed in 8 : (d), for if one atom is placed in xyz there is another one in $xy\frac{1}{2} - z$, and the distance between the two oxygen atoms in the c direction is only $\frac{1}{2}c = 1.43 \text{ \AA}$. By placing the oxygen atoms in two fourfold positions in 4 : (c), one arrives at a very feasible arrangement of these around the manganese atoms, six oxygen atoms forming an octahedron with a manganese atom at its centre. This is a coordination structure of the same kind as is found in pyrolusite. The x and y parameters of the oxygen atoms were determined, and to give a good agreement between the values observed and calculated, the parameters of the manganese atoms had to be adjusted a little. The following arrangement was arrived at:

4 Mn	in 4 : (c)	with $2\pi x_1 = 8^\circ$	and $2\pi y_1 = 49^\circ$	where $x_1 = 0.022$, $y_1 = 0.136$
4 O_1	in 4 : (c)	» $2\pi x_2 = 120^\circ$	and $2\pi y_2 = 99^\circ$	» $x_2 = 0.333$, $y_2 = 0.275$
4 O_2	in 4 : (c)	» $2\pi x_3 = -76^\circ$	and $2\pi y_3 = -12^\circ$	» $x_3 = -0.211$, $y_3 = -0.033$

A projection of the structure upon (001) is shown in Fig. 1 a.

Every manganese atom is surrounded by six oxygen atoms distributed at the corners of a distorted octahedron. Two oxygen atoms are at a distance of 1.86 \AA , two at 1.92 \AA , one at 1.91 \AA and one at 1.89 \AA , which gives an average Mn—O distance of 1.89 \AA . The shortest Mn—Mn distance is 2.91 \AA .

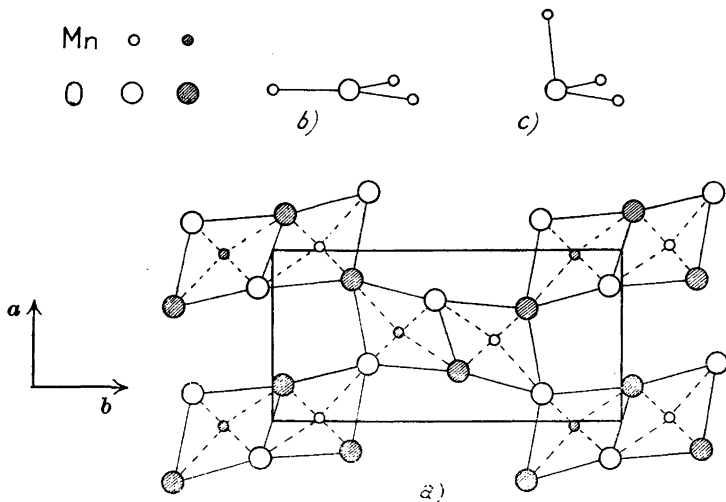


Fig. 1. Ramsdellite, orthorhombic MnO_2 . a) Projection upon (001) at the level of $\frac{1}{4}c$. The filled circles indicate the atoms at the level of $\frac{3}{4}c$. b) The arrangement of the Mn atoms around the O_1 atoms. c) The arrangement of the Mn atoms around the O_2 atoms.

Every oxygen atom is surrounded by three manganese atoms, but there is a difference in the way in which these are arranged around the O_1 and O_2 atoms. The O_1 atom is at the centre of an almost equilateral triangle, which has the metal atoms at its corners, Fig. 1 b. This is like the arrangement in rutile. The O_2 atom is placed at the apex of a trilateral pyramid, the base corners of which hold Mn atoms, Fig. 1 c. The shortest O — O distance is 2.48 Å, which seems very short but not improbable, as will be seen later.

The structure is built up of distorted oxygen octahedra, each with four shared edges. The distortion is due to a contraction of the shared edges, a fact which Pauling^{6,7} has pointed out for all TiO_2 structures. I cite from Pauling⁶, p. 247: »Just such a distortion is to be expected, for the Coulomb repulsion of the two quadrivalent metal ions brought near each other when an edge is shared will cause the titanium — titanium distance to increase until the repulsion of the two oxygen ions defining the shared edge becomes large enough to counteract the effect.» The octahedra in the structure under consideration are linked together by sharing edges in two different ways:

a) In the direction of the c -axis the octahedra are linked together by sharing opposite edges, thus producing continuous strings running in the c direction.

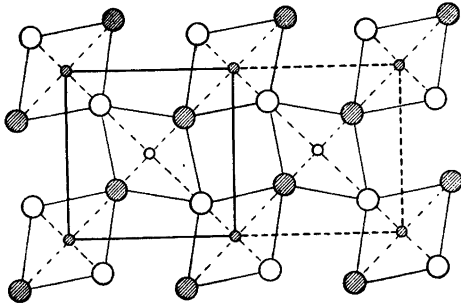


Fig. 2. Pyrolusite, tetragonal MnO_2 . Projection upon (001) at zero level. The filled circles indicate atoms at the level $\frac{1}{2}c$.

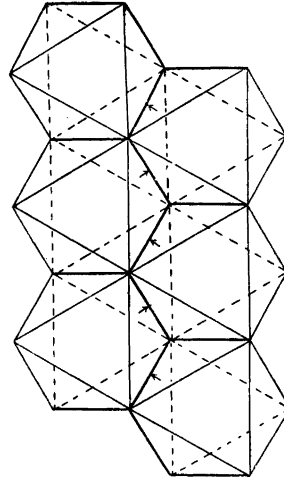


Fig. 3. A double string of undistorted octahedra. Shared edges are drawn in thick lines, and the edges by which two single strings are linked together are indicated by arrows.

b) Two such strings are linked together, one string being displaced half of the c -axis in relation to the other, so that an octahedron from one string shares an edge with each of two octahedra from the other string.

Under a) two manganese ions are brought together and cause a contraction of the shared edge. The O — O distance defining this shared edge is 2.58 Å. Under b) three manganese ions repel each other and the contraction of the shared edges is still larger with the O — O distance of 2.48 Å. Fig. 3 shows two strings of undistorted octahedra linked together in the way just described. The shared edges are drawn in thick lines and those shared between octahedra from two different strings are marked with arrows as well. To complete the structure the octahedra in the double strings are connected with octahedra from other double strings by sharing the corners that do not belong to the edges with the largest contraction.

For the Weissenberg photographs the observed and calculated intensities are given in Table 1. They show good agreement except for a few reflections. Thus 120 and 140, which have almost the same calculated intensities — 3.3 and 3.8 resp — show very different intensities when observed on the photograph of the zero level, with the c axis as the rotation axis, where 140 is much stronger than 120. On the photograph, however, of the first level, with the a axis as the rotation axis, they have about equal intensities, in accordance with the calculated values. For the reflection 101 a similar discrepancy is observed. The photograph from the first level, around the (100) direction,

Table 1: Weissenberg photographs of ramsdellite, orthorhombic MnO_2 . Comparison between observed and calculated intensities. Fe-K radiation.

<i>hkl</i>	<i>I</i> obs.	<i>I</i> calc.	<i>hkl</i>	<i>I</i> obs.	<i>I</i> calc.	<i>hkl</i>	<i>I</i> obs.	<i>I</i> calc.
020	w. +	4.9	340	w.	0.9	231	w.	3.3
040	st.	14	350	m. +	6.5	241	v.w. -	0.6
060	w.	2.3	360	m. +	6.1	251	—	0.0
080	st.	13	370	v.st.	57	261	w.	6.0
						271	—	0.1
110	v.st. +	170	400	st.	15			
120	w.	3.3	410	m.	5.9	301	m.	5.6
130	v.st.	48	420	v.w. -	0.1	311	st.	15
140	m.	3.8	430	—	0.0	321	v.w.	0.1
150	w.	2.8	440	st.	24	331	w.	2.4
160	v.w. -	0.1				341	w.	1.1
170	st.	12	021	v.st.	39	351	m.	7.0
180	m.	3.4	041	w.	3.0	361	w.	1.2
190	w.	1.5	061	v.st.	31			
			081	w. +	5.0	411	m.	6.7
200	st.	18				421	st.	25
210	—	0.0	101	v.w.	0.7			
220	w.	1.9	111	st.	23	002	v.st.	39
230	m.	5.5	121	st.	11	022	v.w.	0.4
240	v.st.	32	131	st.	14	042	m.	14
250	w.	1.6	141	v.w. -	0.4	062	w.	3.0
260	w.	2.6	151	st.	20			
270	v.w. -	0.1	161	v.w. -	0.2	112	st.	9.4
280	st.	22	171	w.	2.0	122	w.	0.5
			181	v.w.	0.8	132	st.	12
310	w.	3.3				142	w.	0.9
320	w.	2.2	211	v.w. -	0.3	152	w.	1.5
330	st.	11	221	v.st.	28	162	v.w. -	0.1

v.w. = very weak, w. = weak, m. = medium, st. = strong, v.st. = very strong.

shows a strong spot, while that from the first level, around the (001) direction, shows a very weak spot, which is in agreement with the calculated intensity, 0.7. Such anomalies must be due to imperfections of the crystal.

In Table 2 the values of the powder photographs are registered. The agreement between observed and calculated intensities is not so good as for the Weissenberg photographs. The divergences, however, are of a systematic nature. Thus the reflections $0k0$ and $1k0$ are much more intense than the other reflections. Comparing for instance 121 and 140, which have about the same observed intensities and angles of reflection close to each other,

Table 2. Powder photographs of ramsdellite, orthorhombic MnO_2 . Comparison between observed and calculated $\sin^2\Theta$ values and intensities. Fe-K radiation.

<i>hkl</i>	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	<i>I</i> obs.	<i>I</i> calc.	<i>hkl</i>	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	<i>I</i> obs.	<i>I</i> calc.
120	0.0885	0.0892	m.	9.5	340	—	0.5848	—	0.9
130	0.1430	0.1437	v.st.	104	132	0.6010	0.6003	w.	25
021	0.1569	0.1577	st.	77	331	—	0.6226	—	4.8
101	—	0.1596	—	0.1	042	—	0.6310	—	15
111	0.1702	0.1706	st.	92	202	—	0.6390	—	7.4
040	0.1739	0.1744	st.	14	212	—	0.6499	—	0.0
200	0.1825	0.1824	v.w.—	16	142	—	0.6764	—	1.8
210	—	0.1933	—	0.0	222	—	0.6826	—	0.7
121	0.2028	0.2033	st.	40	350	—	0.6829	—	6.6
140	0.2196	0.2200	st.	6.5	261	0.6873	0.6889	v.w.	12
220	—	0.2250	—	3.4	171	—	0.6938	—	3.3
131	0.2569	0.2578	st.	45	080	0.6983	{0.6976 0.6989}	w. +	{6.9 2.3}
230	0.2798	0.2805	m.	16	341				
041	0.2879	0.2885	v.w.	4.6	270	—	0.7165	—	0.1
211	—	0.3074	—	0.9	400	—	0.7297	—	6.8
150	0.3171	0.3181	w. +	3.5	232	—	0.7371	—	4.5
141	—	0.3341	—	1.0	410	—	0.7406	—	6.8
221	0.3401	0.3401	st.	85	180	0.7449	0.7432	w.	3.1
240	0.3567	0.3568	st.	44	420	—	0.7733	—	0.1
060	0.3919	0.3924	w.	1.9	152	—	0.7747	—	4.1
231	0.3948	0.3946	w.	10	351	—	0.7970	—	13
310	—	0.4213	—	4.8	360	—	0.8028	—	5.6
160	—	0.4380	—	0.1	081	—	0.8117	—	5.9
151	0.4319	0.4322	st.	53	242	0.8143	0.8141	w. +	56
320	—	0.4540	—	2.6	430	—	0.8278	—	0.0
250	—	0.4549	—	1.9	271	—	0.8306	—	1.0
002	0.4568	0.4566	m.	24	062	—	0.8490	—	2.8
241	—	0.4709	—	1.4	411	—	0.8547	—	12
022	—	0.5002	—	0.4	181	—	0.8573	—	1.6
061	0.5060	0.5065	st.	{34	312	—	0.8779	—	9.5
330		0.5085		{12	280	0.8809	0.8800	w.	17
112	0.5130	0.5131	v.w.	21	421	—	0.8874	—	37
301	0.5254	0.5245	v.w.—	6.3	162	—	0.8946	—	0.1
311	0.5358	0.5354	w.	35	440	—	0.9041	—	19
122	—	0.5458	—	1.3	322	—	0.9108	—	7.3
161	—	0.5521	—	0.5	252	—	0.9115	—	5.7
321	—	0.5681	—	0.2	361	—	0.9169	—	3.0
251	—	0.5690	—	0.0	190	—	0.9285	—	1.5
260	—	0.5748	—	2.8	431	—	0.9419	—	18
170	0.5794	0.5796	m.	13	370	0.9445	0.9445	w.diff.	40

v.w. = very weak, w. = weak, m. = medium, st. = strong, v.st. = very strong, diff. = diffuse.

Table 3. Comparison between ramsdellite, a synthetical product of γ - MnO_2 and pyrolusite. Cr-K radiation. The β -reflections are omitted, except when they coincide with α -reflections.

Ramsdellite				γ - MnO_2			(MnO _{1.987})		Pyrolusite		
<i>d</i>	<i>hkl</i>	Sin ² θ obs.	<i>I</i> obs.	<i>hkl</i>	Sin ² θ obs.	<i>I</i> obs.	<i>hkl</i>	<i>h2kl</i>	Sin ² θ obs.	<i>I</i> obs.	
4.10	110	0.0777	v.st.	110	0.08	st.diff.					
3.232	120	0.1250	w.	120	0.13	v.w.—	110	120	0.1346	st.	
2.535	130	0.2001	v.st.								
2.436	021	0.2200	st.	021	0.2213	st.	011	021	0.2259	m.	
2.343	111	0.2379	m.	111}	0.2400	m.(br.)					
2.329	040	0.2429	m.	040}				020	040	0.2716	w.
2.143	121	0.2843	st.	121	0.2878	st.	111	121	0.2954	st.	
2.058	140	0.3080	st.	140	0.3070	w.	120	140	0.3393	m.	
1.903	131	0.3609	st.	131	0.38	v.w.					
1.796	041	0.4044	w.								
1.713	150	0.4450	m.								
1.670	141	0.4688	v.w.								
1.656	221	0.4767	st.	221	0.4885	st.(br.)	211	221	0.4989	v.st.	
1.616	240}	0.5002	v.st.	240	0.5091	m.	220	240	0.5427	st.	
β 151}											
1.542	060	0.5490	v.w.								
1.537	231	0.5533	w.								
1.479	151	0.6050	v.st.	151	0.59	w.diff.					
1.429	002	0.6398	m.	002	0.6459	m.	002	002	0.6374	st.	
1.357	330}	0.7088	v.st.				130	160	0.6790	m.	
	061}										
1.348	112	0.7190	w.								
1.320	311	0.7510	w.+								
1.270	170	0.8108	m.								
1.246	132	0.8416	m.								
1.216	042	0.8841	w.—								

v.w. = very weak, w. = weak, m. = middle strong, st. = strong, v.st. = very strong, br. = broad, *d*. = spacings in kX.

we find that the calculated intensity for 121 is 40 and that for 140 is only 6.5. Similarly the calculated intensities for $0k0$ and $1k0$ are in general only one sixth of those calculated for the general reflections with the same observed intensities. This must be due to preferred orientations of the crystallites, in spite of the fact that the material was well ground before it was used for powder photographs. Why 280 appears — with a calculated intensity of 17 — and not 421, with a calculated intensity of 37, is a little difficult to explain, for there does not seem to be any constant strengthening of the $2k0$ reflections. Probably overmuch importance should not be attached to this fact, as the

last part of the film from the outer focusing camera is rather diffuse, especially for reflections with $\sin^2\theta$ values greater than 0.7.

Table 3 contains X-ray data for a synthetically prepared γ - MnO_2 . The products obtained all had very similar powder patterns and the lines were not so sharp that it was possible to decide whether differences in the observed $\sin^2\theta$ values were due to changes in the cell dimensions or should be ascribed to different measurements of the lines. Therefore, data for only one product are shown in the table. This γ - MnO_2 was prepared by oxidising a solution of MnSO_4 with ammonium persulphate. The precipitate was well washed with hot water and then boiled for ten hours with sulphuric acid, washed and dried at 115°C till constant weight was obtained. The proportions of manganese and available oxygen were determined. The following values were obtained: MnO — 79.75 % and O — 17.70 %, giving the total 97.45%. The missing per cents are probably water which was not determined, as it was not possible to decide whether it enters the structure or is absorbed water. Without counting the water, the formula is $\text{MnO}_{1.967}$, and the corresponding value for ramsdellite is $\text{MnO}_{1.971}$. As a comparison, the observed reflections of ramsdellite are given in Table 3, together with the intensities and the $\sin^2\theta$ values for unfiltered Cr-K radiation. The β -reflections are omitted except when they coincide with α -reflections. In the pattern of γ - MnO_2 we do not find strong reflections from the planes 130, 131, 151 and 330—061 as are found in the pattern of ramsdellite. There is only a shading of the film where the reflections might be expected. The sharp reflections that appear are the very ones that are common for ramsdellite and pyrolusite, indexed with a double b -axis. This is elucidated in Table 3, in which next to the column with the correct indices of pyrolusite, there is a column where all the k -indices are doubled. The cell dimensions of the three substances are:

	a	b	c
pyrolusite	4.40 Å	4.40 Å	2.87 Å
γ - $\text{MnO}_{1.967}$	4.43	9.36	2.85
ramsdellite	4.53	9.27	2.86

It is probable that the synthetic γ - MnO_2 is an intermediate product between pyrolusite and ramsdellite and that the γ - MnO_2 here prepared is very closely related to pyrolusite, while the γ - MnO_2 prepared by Cole and co-workers³ has taken a further step towards ramsdellite, for in their pattern 130 also appears. A projection of pyrolusite upon (001) is shown in Fig. 2.

When the structure of ramsdellite had already been determined Mr. Fleischer drew my attention to the remarkable similarity that Mr. Richmond

had found between the powder patterns of ramsdellite and diaspore, AlHO_2 . A closer comparison shows that as a matter of fact ramsdellite belongs to the same type of structure — EO_2 — as diaspore. They have the same space group, D_{2h}^{16} , almost the same cell dimensions, and their parameters differ but little, as can be seen from the table below, where the corresponding values for goethite are also listed. The values for diaspore and goethite are from Hoppe ^{8,9}.

		Parameters								
		<i>a</i>	<i>b</i>	<i>c</i>	x_{Mn}	y_{Mn}	x_{O_1}	y_{O_1}	x_{O_2}	y_{O_2}
ramsdellite	MnO_2	4.53 Å	9.27 Å	2.87 Å	+0.022	0.136	0.17	−0.23	−0.21	−0.033
diaspore	AlHO_2	4.42	9.44	2.84	−0.048	0.146	0.29	−0.20	−0.20	−0.056
goethite	FeHO_2	4.59	10.00	3.03	−0.045	0.146	0.31	−0.20	−0.20	−0.047
groutite	MnHO_2	4.56	10.70	2.85						

It is interesting to compare the interatomic distances in the structures of ramsdellite and diaspore, particularly as the Mn^{4+} and the Al^{3+} ions are of the same size. All the corresponding interatomic distances except one are equal; the one exception being the distance between oxygen atoms marked A and B in Fig. 1 a. For diaspore this distance is only 2.65 Å, which is very short to be between oxygen atoms belonging to different octahedra. Ewing ¹⁰ explained this short distance as due to a hydrogen bond and Hoppe ⁹ came to the same conclusion. For ramsdellite which does not contain any hydrogen atoms the distance A—B is 3.34 Å, which is quite normal. The divergency of the two distances A—B in diaspore and ramsdellite may be another proof that the proposed positions for the hydrogen atoms in diaspore are correct. Anyhow, it is evident that the hydrogen atoms are not essential for the structure type of diaspore.

Recently Gruner ¹¹ has described a new mineral, groutite, MnHO_2 , which he preliminarily determined to belong to the diaspore-goethite group. Cell dimensions for groutite are listed in the table above. Further investigation will show if this mineral really has the same structure as diaspore, in which case ramsdellite, MnO_2 , and groutite, MnHO_2 , are also isostructural, rather a unique occurrence.

SUMMARY

The structure of ramsdellite, MnO_2 , has been investigated. The symmetry is orthorhombic and the cell dimensions are $a = 4.533$ Å, $b = 9.27$ Å and $c = 2.866$ Å. Possible space groups are D_{2h}^{16} and C_{2v}^9 . Good agreement between observed and calculated values is found for the following arrangement of the atoms in D_{2h}^{16} — $Pbnm$

$$\begin{array}{lll}
 4 \text{ Mn in } 4:(c): 2\pi x_1 = & 8^\circ & 2\pi y_1 = 49^\circ \\
 4 \text{ O}_1 \text{ in } 4:(c): 2\pi x_2 = & 120^\circ & 2\pi y_2 = 99^\circ \\
 4 \text{ O}_2 \text{ in } 4:(c): 2\pi x_3 = & -76^\circ & 2\pi y_3 = -12^\circ
 \end{array}$$

Each manganese atom is surrounded by six oxygen atoms distributed at the corners of an octahedron with an average Mn — O distance of 1.89 Å. Each oxygen atom is surrounded by three manganese atoms. The oxygen octahedra are linked together by sharing edges, thus producing double strings running in the *c* direction; in pyrolusite there are single strings. By sharing corners the octahedra are further linked together to complete the structure. The relations between pyrolusite, γ -MnO₂ and ramsdellite are shown and cell dimensions are given for a synthetically prepared γ -MnO₂.

A comparison between the structures of ramsdellite and diaspore is also made, and indicates that they belong to the same type of structure, as well as the new mineral groutite MnHO₂. The contraction between oxygen atoms in diaspore, which is due to the hydrogen bond, is not found in ramsdellite.

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