

α -Manganese(III) Oxide — a C-Type Sesquioxide of Orthorhombic Symmetry

ROLF NORRESTAM

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The crystal structure of synthetic α -manganese(III) oxide has been studied on the basis of three-dimensional X-ray single-crystal diffractometer data registered with $\text{MoK}\alpha$ radiation. Least-squares refinement of the structure has been carried out to a final R value of 3%. The structure which clearly deviates from the body-centered cubic symmetry, generally assigned to the C-type sesquioxides, is primitive orthorhombic ($Pbca$). The structural details are discussed and compared with those of scandium oxide (C-type of $Ia\bar{3}$ symmetry). — A procedure is described for using X-ray data to estimate the extent of twinning in composite crystals.

A cubic C-type sesquioxide structure has been assigned to $\alpha\text{-Mn}_2\text{O}_3$ by Zachariassen¹ and by Pauling and Shappel² on the basis of X-ray powder data. Recent studies^{3,4} applying neutron diffraction powder techniques have been reported to confirm this type of structure. X-Ray single-crystal structure investigations have been performed for the mineral bixbyite^{1,4,5} which represents a solid solution of Fe_2O_3 in Mn_2O_3 . According to these investigations bixbyite also adopts the cubic C-type structure. The reported unit-cell dimensions for bixbyite⁵ are $a = 9.40 \text{ \AA}$ and for $\alpha\text{-Mn}_2\text{O}_3$ ⁶ $a = 9.411 \text{ \AA}$. However, this small difference of unit-cell dimensions for bixbyite and $\alpha\text{-Mn}_2\text{O}_3$ does not indicate that the iron content of bixbyite is small⁷ and in fact a composition of about FeMnO_3 has been obtained¹ by chemical analysis.

Due to the limited knowledge of the structural chemistry of trivalent manganese, in particular in simple binary compounds, and the general interest in the structural behaviour of a high-spin d^4 -ion,⁸ it was considered worthwhile to undertake a detailed structural study on the basis of single-crystal data obtained from a pure $\alpha\text{-Mn}_2\text{O}_3$ specimen.

PREPARATION

Several investigations (*e.g.* Refs. 9–13) of the system $\text{Mn}-\text{O}$ have shown that MnO_2 decomposes to $\alpha\text{-Mn}_2\text{O}_3$, when heated at 600–800°C in air; $\alpha\text{-Mn}_2\text{O}_3$ in turn decomposes to tetragonal Mn_3O_4 at 850–900°C in air. In the present study a powder sample of

α - Mn_2O_3 was prepared by decomposition of commercial MnO_2 (Baker's analyzed) at 800°C in air. The weight loss observed corresponded to the composition $\text{MnO}_{1.495}$ of the product. From the equilibrium studies by Hahn and Muan¹² on the reaction $6\alpha\text{-Mn}_2\text{O}_3 = 4\text{Mn}_3\text{O}_4 + \text{O}_2$ the equilibrium oxygen pressure at 1050°C would be 2.6 atm. For this reason the following procedure was used for preparing crystals of $\alpha\text{-Mn}_2\text{O}_3$. The powder sample of $\alpha\text{-Mn}_2\text{O}_3$ was annealed in a sealed silica tube at about 1050° for a week, whereupon the heat treatment was discontinued by quenching the tube in cold water. The sample was then powdered and annealed again as above. This heat treatment was repeated until single crystals of a size suitable for an X-ray investigation were formed. The obtained crystalline sample was then annealed at 800°C in air for a week, to ensure a stoichiometric composition of the material.

CRYSTAL SELECTING PROCEDURE AND X-RAY DATA COLLECTING

Weissenberg photographs were taken for several crystals of $\alpha\text{-Mn}_2\text{O}_3$, using $\text{CuK}\alpha$ radiation. On these photographs weak reflections with $h+k+l$ odd were observed, indicating that the lattice of $\alpha\text{-Mn}_2\text{O}_3$ cannot be body-centered as is the case for other sesquioxides having the C-type structure (space group $Ia\bar{3}$), e.g. Sc_2O_3 .¹⁴ When examining the reflections with high values of $\sin\theta$, recorded on the Weissenberg photographs, it was observed that these reflections showed a small splitting into several components (apart from those due to the α_1 - α_2 splitting of the $\text{CuK}\alpha$ radiation). Further it was observed that the ratios of the intensities for pairs of reflections of the type hkl and khl often varied markedly for different crystals. This indicated that twinning was occurring and that special attention must be paid to it. It was found impossible to apply microscopical techniques for testing the quality of the very small irregularly shaped opaque crystals. For this reason the procedure described below was applied to intensity measurements with a single-crystal diffractometer, to find a crystal with a negligible amount of twinning.

The problem is to test crystals for usefulness for single crystal studies by estimating the maximum amount of twinning when lattice points of the twins coincide. It is presumed that only the intensities for the twinned crystal are known.

Consider pairs of reflections whose intensities are related to each other by such twinning. Suppose that the observed intensities for such pairs are I_1 and I_2 , and that the corresponding unknown intensities for an untwinned crystal are i_1 and i_2 , respectively. Now assume as an *approximation* that the following relations are valid:

$$\begin{aligned} kI_1 &= (1-t)i_1 + ti_2 & \text{where } 0 \leq t \leq \frac{1}{2} \\ kI_2 &= (1-t)i_2 + ti_1 \end{aligned} \quad (1)$$

t is a measure of the extent of twinning and k is a scale factor between the intensities of the two crystals.

If one arbitrarily considers only such pairs of reflections for which $i_1 \geq i_2$ and hence $I_1 \geq I_2$, because of the definition of t , the following expressions are valid:

$$\begin{aligned} i_2 &= \alpha i_1 & \text{where } 0 \leq \alpha \leq 1 \\ I_1 &= pI_2 & \text{where } p \geq 1 \end{aligned}$$

(Because of the twinning $p \alpha \leq 1$). The relations (1) can now be written:

$$\begin{aligned} kI_1 &= i_1 [1 - t(1-\alpha)] \\ kI_2 &= i_1 [\alpha + t(1-\alpha)] \end{aligned}$$

By putting in $I_1 = pI_2$, one obtains after division and rewriting

$$t = (1 - p\alpha)/(1 - \alpha) \times 1/(p + 1)$$

Since $p \leq 1$ and $0 \leq p\alpha \leq 1$, and hence $0 \leq 1 - p\alpha \leq 1 - \alpha$, the following relations are valid:

$$\begin{aligned} t &\leq 1/(p + 1) \text{ or} \\ t &< 1/p \end{aligned} \quad (2)$$

i.e. $1/p$ is a measure of the maximum extent of this type of twinning in such cases where the approximation is good. To be able to conclude only from X-ray diffraction data that this type of twinning is negligible, one must find suitable pairs of reflections that give high values of p .

No splitting of reflections having high values of $\sin \theta$ was observed for the finally selected crystal. The unit-cell dimensions of this crystal calculated by the least-squares method from determinations of 2θ -values at 27.5°C for reflections along the directions [100], [010], and [001] using a single-crystal diffractometer with receiver slit (0.02° wide) gave

$$\begin{aligned} a &= 9.4118 \pm 0.0008 \text{ \AA} \\ b &= 9.4177 \pm 0.0007 \text{ \AA} \\ c &= 9.4233 \pm 0.0007 \text{ \AA} \end{aligned}$$

No deviations from 90° by the lattice angles could be detected. (Very recently Geller *et al.* have reported that $\alpha\text{-Mn}_2\text{O}_3$ does not have higher than orthorhombic symmetry.¹⁵)

It is to be noticed that applying the same technique to the determination of the unit-cell parameters for the cubic Sc_2O_3 , gave $a = 9.8489 \pm 0.0008 \text{ \AA}$, $b = 9.8490 \pm 0.0011 \text{ \AA}$, and $c = 9.8487 \pm 0.0007 \text{ \AA}$.

The small differences of the axial lengths thus accounts for the observed splitting of reflections given by twinned $\alpha\text{-Mn}_2\text{O}_3$ crystals, and it also means that all components (due to twinning) of a reflection are registered as a single reflection when measuring the intensities with the diffractometer. This fact justifies an application of the method described above for estimation of the maximum extent of twinning. In Table 1, intensities of selected reflections

Table 1. Selected intensities from the crystal used for collecting the intensity data. The 2θ - θ scan technique with a scan interval of 2° was used.

hkl	I_0 counts/256	hkl	I_0 counts/256
8 4 6	157	4 5 0	0.6
4 8 6	0.4	5 0 4	11.7
8 6 4	0.7	0 4 5	13.8
6 8 4	165	8 3 0	16.9
6 4 8	0.0	3 0 8	0.7
4 6 8	167	0 8 3	20.9

are given, and by applying the relations (2) to these it can be seen that twinning is negligible.

Integrated intensities of X-ray reflections from the selected crystal were obtained by means of the diffractometer. This was equipped with a General Electric single-crystal orienter ("Goniostat"), a scintillation counter with pulse height selection equipment, and an electronic timer. The radiation used

was $\text{MoK}\alpha$ filtered through a niobium foil (0.052 mm thick). The $2\theta - \theta$ scan technique¹⁶ was applied and a scanning interval of 2° was used. The background intensity was calculated as the average of the background intensities at each end of the scan interval. The intensities of the 1290 observable reflections within the range $0 < \sin^2 \theta_{hkl} \leq 0.6$ in the unique eighth of the reciprocal lattice were collected. This means that approximately 30 % of the reflections within this range were observable, systematic extinctions being disregarded.

The intensities of the reflections showed the Laue symmetry to be mmm . The observed systematic absences of reflections are those characteristic of the orthorhombic space group $Pbca$. Due to the low intensities of the reflections with $h+k+l$ odd, this assignment of symmetry is statistically not strongly substantiated. However, this space group was tentatively adopted for the structural study and fully supported by the outcome of the investigation.

The net intensities were corrected for Lorentz-polarization and absorption effects. In the calculation of absorption factors a linear absorption coefficient with the value¹⁷ $\mu = 123.5 \text{ cm}^{-1}$ was used. The crystal had the dimensions $0.045 \times 0.055 \times 0.09 \text{ mm}^3$ and when correcting the intensities for absorption the transmission factors varied from 0.46 to 0.58.

REFINEMENT OF THE STRUCTURE

As starting coordinates for the refinement those given by Fert³ for $\alpha\text{-Mn}_2\text{O}_3$, derived from neutron powder diffraction data, were used. The structure was described by Fert as cubic with the space group $Ia3$, so the point positions of $Ia3$ had to be resolved into the corresponding point positions of the orthorhombic space group $Pbca$, (cf. Table 2). These coordinates were in

Table 2. Starting coordinates used in the least-squares refinement obtained by rewriting the coordinates given by Fert.³ The standard deviations are those given by Fert for the space groups $Ia3$.

		Space group $Pbca$ (No. 61 [17]) Cell content $16 \text{ Mn}_2\text{O}_3$ 8 Mn in $4(a)$ and $4(b)$ 24 Mn in $3 \times 8(c)$ 48 O in $6 \times 8(c)$					
		x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Mn	1	0		0		0	
	2	$\frac{1}{2}$		$\frac{1}{2}$		$\frac{1}{2}$	
	3	0.2847	0.0008	0		$\frac{1}{4}$	
	4	0		$\frac{1}{2}$		0.2847	0.0008
	5	$\frac{1}{2}$		0.2847	0.0008	0	
O	6	0.128	0.0005	0.147	0.001	0.917	0.0005
	7	0.147	0.001	0.917	0.0005	0.128	0.0005
	8	0.917	0.0005	0.128	0.0005	0.147	0.001
	9	0.628	0.0005	0.647	0.001	0.417	0.0005
	10	0.647	0.001	0.417	0.0005	0.628	0.0005
	11	0.417	0.0005	0.628	0.0005	0.047	0.001

satisfactory concordance with the Patterson sections and projections obtained from the present investigation. Estimated values for the scale factor and the individual isotropic temperature factors together with these coordinates, were then used as starting parameters in a least squares refinement by means of program No. 6023.¹⁸ In the refinement the $|F_o|$'s were weighted according to Cruickshank's weighting procedure, *i.e.* $w = 1/(a + |F_o| + c|F_o|^2)$, using the values $a = 100$ and $c = 0.005$. The atomic scattering curves^{19,20} for Mn^{3+} and O^{2-} , and the real part of the dispersion correction¹⁷ for Mn^{3+} were used in the structure factor calculations.

The symmetry assigned by Fert (*e.g.* $Ia\bar{3}$) was then lowered during the refinement to obtain the symmetry of the space group $Pbca$, following a procedure similar to that described by Åsbrink and Kihlberg²¹ for revealing minor deviations from centrosymmetry. A final discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ of 0.072 was obtained, when all the observed 1290 reflections were included. Omitting 44 of the strongest reflections caused the

Table 3. Atomic coordinates, isotropic temperature factors in Å² and standard deviations for α - Mn_2O_3 , obtained by least-squares refinement using the block diagonal matrix approximation and isotropic temperature factors.

Atom No.	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Mn 1	0		0		0		0.268	0.013
2	$\frac{1}{2}$		$\frac{1}{2}$		$\frac{1}{2}$		0.342	0.013
3	0.28467	0.00010	0.99389	0.00012	0.25339	0.00021	0.457	0.008
4	0.00552	0.00013	0.24558	0.00015	0.28493	0.00010	0.448	0.008
5	0.25195	0.00019	0.28527	0.00010	0.00076	0.00021	0.493	0.008
O 6	0.13316	0.00063	0.15044	0.00062	0.91362	0.00067	0.637	0.065
7	0.14572	0.00067	0.91458	0.00065	0.12791	0.00066	0.729	0.068
8	0.92074	0.00059	0.12344	0.00055	0.14485	0.00062	0.442	0.056
9	0.62523	0.00062	0.64525	0.00062	0.41825	0.00066	0.612	0.062
10	0.64727	0.00062	0.41990	0.00059	0.62763	0.00061	0.550	0.061
11	0.40935	0.00063	0.63512	0.00060	0.64971	0.00068	0.624	0.064

Table 4. Atomic coordinates and standard deviations obtained by full matrix least-squares refinement with anisotropic temperature factors.

Atom No.	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Mn 1	0		0		0	
2	$\frac{1}{2}$		$\frac{1}{2}$		$\frac{1}{2}$	
3	0.28469	0.00007	0.99377	0.00012	0.25240	0.00025
4	0.00448	0.00013	0.24602	0.00015	0.28494	0.00007
5	0.25285	0.00015	0.28531	0.00006	0.00134	0.00016
O 6	0.13378	0.00059	0.15082	0.00048	0.91546	0.00071
7	0.14472	0.00060	0.91494	0.00049	0.12817	0.00058
8	0.91968	0.00065	0.12400	0.00045	0.14574	0.00081
9	0.62466	0.00063	0.64529	0.00053	0.41718	0.00066
10	0.64856	0.00066	0.42004	0.00044	0.62737	0.00070
11	0.41156	0.00063	0.63450	0.00047	0.64916	0.00090

Table 5. Anisotropic temperature factors and standard deviations multiplied by 10^5 .

$$T = \exp(-h^2b_{11} - k^2b_{22} - l^2b_{33} - hkb_{12} - hlb_{13} - klb_{23})$$

Atom No.	b_{11}	$\sigma(b_{11})$	b_{22}	$\sigma(b_{22})$	b_{33}	$\sigma(b_{33})$	b_{12}	$\sigma(b_{12})$	b_{13}	$\sigma(b_{13})$	b_{23}	$\sigma(b_{23})$	
Mn	1	168	32	104	26	36	24	21	20	6	19	-27	13
	2	30	24	89	25	163	31	-18	18	-1	19	30	13
	3	100	3	191	5	141	4	20	14	-1	20	-120	10
	4	210	5	149	4	93	3	-146	8	-41	19	-7	13
	5	135	4	107	3	198	4	-6	22	-124	7	-43	15
O	6	183	37	155	31	262	57	9	60	-229	74	147	68
	7	128	41	276	36	117	52	32	67	-16	88	-185	65
	8	258	40	160	29	77	38	-22	57	-69	69	-38	55
	9	177	35	163	28	185	50	-45	53	-49	72	-178	67
	10	159	43	124	30	345	76	-122	64	13	104	-110	69
	11	202	37	208	32	214	53	-240	65	-70	67	63	66

Table 6. Weight analysis. w = weighting factor. $\Delta = |F_o| - |F_c|$

Interval $ F_o $	No. of reflections	$w \Delta^2$ normalized
0 - 14.6	8	0.74
14.6- 29.3	121	1.51
29.3- 43.9	415	1.15
43.9- 58.6	232	0.88
58.6- 73.2	158	0.91
73.2- 87.9	87	0.42
87.9-102.5	89	0.85
102.5-117.2	60	1.01
117.2-131.8	40	0.80
> 131.8	63	0.84

R -value to become 0.055 and produced shifts in some parameters larger than their standard deviations. For this reason a correction for secondary extinction was made according to the expression derived by Zachariasen.²² A refinement including all the 1290 reflections then gave the R -value 0.054 and the parameters listed in Table 3.

Anisotropic temperature factors were then introduced into the structure refinement by means of the modified program No. 384,¹⁸ whereby the R -value decreased to 0.032 after four cycles. However, large discrepancies appeared for the strongest reflections. By excluding the 17 strongest reflections an R -value of 0.030 was obtained and the standard deviations and the weight analysis improved slightly. The differences in the parameters thus obtained did not exceed the standard deviations, so it was not considered necessary to perform a further correction for secondary extinction. The final coordinates, temperature factors and normalized weight analysis are given in Tables 4, 5, and 6, respectively. The observed and calculated structure factors are given in Table 7.

Table with 4 columns of data for Mn and O atoms, including coordinates (h, k, l), displacement components (F0, Fc), and thermal parameters. The table is organized into three main sections for Mn atoms and one section for O atoms, each with multiple rows of data points.

The root mean square displacements in Å along the principal axis of thermal motion are listed in Table 8, together with the direction cosines of the principal axis with respect to the unit cell axis. The Jacobi method, for determination of latent roots and vectors for symmetric matrices, was used in the calculation of these.

By comparing the coordinates given in Tables 3 and 4 it is seen that by introducing anisotropic temperature factors into the structure refinement, differences in the coordinates for the manganese atoms of up to about 0.01 Å and for the oxygen atoms of up to about 0.02 Å were obtained. By comparing these shifts with the corresponding standard deviations σ of the coordinates, the shifts are up to 8σ and 4σ, respectively. As regards the deviations from

Table 8. Root mean square displacements (r.m.s.) in Å along principal axes of the ellipsoids of vibration and direction cosines g_1 , g_2 , and g_3 of these axes with respect to the unit cell axes a , b , and c .

Atom No.	r.m.s.	g_1	g_2	g_3
Mn 1	0.087	0.99	0.16	0.01
	0.069	-0.15	0.97	-0.20
	0.039	-0.04	0.19	0.98
2	0.036	0.99	0.15	-0.01
	0.063	-0.15	0.97	-0.19
	0.086	-0.02	0.19	0.98
3	0.065	0.76	-0.40	-0.51
	0.102	0.06	0.83	-0.55
	0.069	0.64	0.39	0.66
4	0.108	0.83	-0.55	-0.09
	0.071	0.39	0.70	-0.59
	0.060	0.39	0.46	0.80
5	0.062	0.65	0.60	0.47
	0.072	-0.57	0.79	-0.22
	0.104	-0.51	-0.13	0.85
O 6	0.057	0.61	-0.54	0.58
	0.087	0.60	0.79	0.11
	0.127	-0.52	0.28	0.81
7	0.075	0.99	-0.09	0.03
	0.120	0.09	0.90	-0.42
	0.058	0.01	0.42	0.91
8	0.109	0.98	-0.07	-0.17
	0.086	0.03	0.97	-0.23
	0.054	0.19	0.22	0.96
9	0.092	0.95	-0.26	-0.17
	0.058	0.31	0.71	0.63
	0.109	-0.04	-0.66	0.75
10	0.094	0.82	-0.52	-0.23
	0.057	0.56	0.81	0.15
	0.127	0.11	-0.25	0.96
11	0.062	0.72	0.69	0.03
	0.124	-0.66	0.67	0.35
	0.094	0.22	-0.27	0.94

cubic symmetry and body-centering for the obtained structure, these can be seen to be significant by comparing the deviations of the coordinates for initially symmetry-related atoms, with their standard deviations (*cf.* Tables 4 and 2).

Fig. 1. The two types of coordination octahedra.



DISCUSSION

The general features of the structure thus arrived at are in agreement with the description given by Pauling and Shappel.² Thus the manganese atoms are six-coordinated by the oxygen atoms in mainly two different ways. These two different types of coordination polyhedra (see Fig. 1), here called the I- and II-octahedron, respectively, correspond to manganese atoms in the point positions 4(*a*) or 4(*b*), and 8(*c*). As Pauling and Shappel pointed out,

Table 9. Manganese-oxygen distances with standard deviations.

Type of octahedron	Atoms No.	Distance with e.s.d. in Å	
I	1-6	2.058	± 0.005
	1-6	2.058	0.005
	1-7	1.989	0.005
	1-7	1.989	0.005
	1-8	1.955	0.006
	1-8	1.955	0.006
I	2-9	1.964	0.006
	2-9	1.964	0.006
	2-10	1.991	0.006
	2-10	1.991	0.006
	2-11	2.067	0.007
	2-11	2.067	0.007
II	3-6	2.192	0.006
	3-7	1.912	0.006
	3-8	2.010	0.006
	3-9	2.306	0.006
	3-10	1.893	0.006
	3-11	1.957	0.006
II	4-6	1.984	0.006
	4-7	2.274	0.005
	4-8	1.918	0.006
	4-9	1.982	0.006
	4-10	2.229	0.006
	4-11	1.878	0.007
II	5-6	1.875	0.006
	5-7	1.962	0.005
	5-8	2.262	0.007
	5-9	1.912	0.006
	5-10	2.011	0.006
	5-11	2.215	0.007

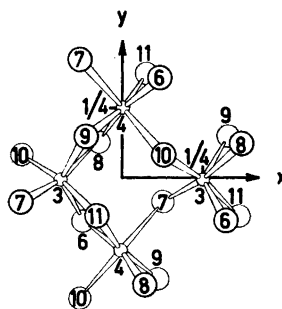
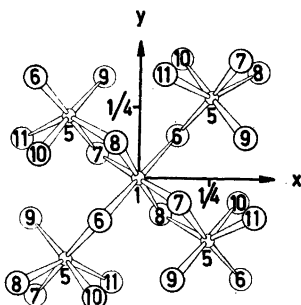


Fig. 2. Slice of a part of the structure, showing some coordination octahedra in the range $-0.15 \leq z \leq 0.15$. The atoms are numbered according to Table 4.

Fig. 3. As Fig. 2, but in the range $0.08 \leq z \leq 0.42$.

each octahedron shares six edges with six surrounding octahedra and the arrangement of this edge sharing is different for the two types of octahedra.

In Table 9 all manganese-oxygen distances within the octahedra are listed together with their calculated standard deviations. The calculation of these distances has been made from the coordinates etc. in Table 4, and in calculating the standard deviations regard was paid to errors in coordinates and cell parameters. The shortest oxygen-oxygen distance obtained is 2.55 Å and the shortest manganese-manganese distance is 3.08 Å. In Figs. 2 and 3, slices of a part of the structure at two different heights are shown.

The great deviations obtained for the manganese-oxygen distances within the coordination octahedra (*cf.* Table 9), may be due to the Jahn-Teller effect. For this reason it seems interesting to make a comparison with the very similar crystal structure of Sc_2O_3 (having the normal C-type sesquioxide structure), since the electronic structure of Sc^{3+} has the closed argon configuration. A refinement of the crystal structure of Sc_2O_3 from single-crystal diffractometer data is described elsewhere.¹⁴ In Table 10 the metal-oxygen distances obtained for $\alpha\text{-Mn}_2\text{O}_3$ and Sc_2O_3 within the two different types of octahedra are listed (*cf.* Fig. 1).

Table 10. Comparison of metal-oxygen distances within the octahedra for Sc_2O_3 ²⁰ and $\alpha\text{-Mn}_2\text{O}_3$.

Type of octahedron	Sc_2O_3		$\alpha\text{-Mn}_2\text{O}_3$	
	Distance in Å	Multiplicity	Distance in Å	Multiplicity
I	2.12	6	1.96–1.99	4
			2.06–2.07	2
II	2.16	2	2.19–2.31	2
	2.12	2	1.96–2.01	2
	2.08	2	1.88–1.92	2

In α - Mn_2O_3 the octahedra are distorted in such a way that four shorter and two longer metal-oxygen bonds are found, while no similar distortion is observed in Sc_2O_3 . In α - Mn_2O_3 the four shorter metal-oxygen bonds lie almost in a plane, while the two other oxygen atoms forming the longer bonds lie on each side of this plane. A possible cause of these distortions of the octahedra is the Jahn-Teller effect which predicts distortion of an octahedral coordination around a high spin d^4 -ion, to produce either two longer bonds and four shorter co-planar ones or four longer coplanar bonds and two shorter ones.⁸ The distortion giving two longer bonds and four shorter ones is the more common and is observed, *e.g.*, for spinels, containing trivalent manganese in the octahedral positions. Thus in ZnMn_2O_4 ²³ the two longer manganese-oxygen distances are 2.27 Å and the four shorter ones are 1.93 Å. In Mn_3O_4 ²³ the corresponding distances are 2.29 Å and 1.93 Å, respectively. These distances agree well with those obtained for the II-octahedra in α - Mn_2O_3 . However, the distortion of the I-octahedra in α - Mn_2O_3 is smaller than expected, but this may be due to spatial considerations.

The calculations were performed on the computers BESK and FACIT EDB of the *Computer Division of the National Swedish Rationalization Agency* and UNIVAC 1107 of the *Norsk Regnesentral*, Oslo, using the program listed in Table 11.

Table 11. List of programs used.

Program No.	Function	Author
6031	Calculates diffractometer settings	Norrestam
6033	Lp-correction, calculates direction cosines of X-rays	Norrestam
6029	Absorption and secondary extinction correction	Werner
6015	Calculates structure factors	Liminga and Olovsson
6014	Fourier synthesis	Liminga and Olovsson
6023	LS-refinement, uses block diagonal approximation with individual, isotropic temperature factors	Åsbrink and Brändén
384	LS-refinement, full matrix including anisotropic temperature factors	Gantzel, Sparks and Trueblood, modified by Rømming for UNIVAC 1107.
6016	Calculates interatomic distances and angles	Liminga and Olovsson
6030	Calculates standard deviations of interatomic distances	Åsbrink and Norrestam

Acknowledgements. The author wishes to express his gratitude to Professor Arne Magnéli for his continuous interest in this study and for many stimulating discussions.

Thanks are due to Dr. S. Åsbrink for suggesting this investigation and for his invaluable advice and suggestions in connection with this work. Dr. C. Rømming is to be thanked for his assistance in the least-squares refinement.

The author is grateful to the *Computer Division of the National Swedish Rationalization Agency* for the use of the computers BESK and FACIT EDB.

The investigation has been supported financially by the *Malmfonden — Swedish Foundation for Scientific Research and Development* and the *Swedish Natural Science Research Council*.

REFERENCES

1. Zachariasen, W. H. *Z. Krist.* **67** (1928) 455.
2. Pauling, L. and Shappell, M. D. *Z. Krist.* **75** (1930) 128.
3. Fert, A. *Bull. Soc. Franc. Minéral. Crist.* **85** (1962) 267.
4. Hase, W. *Physica Status Solidi* III, K. **446** (1963).
5. Dachs, H. *Z. Krist.* **107** (1956) 370.
6. NBS, Standard X-ray Diffraction Powder Pattern (1960).
7. Muan, A. and Sömiya, S. *Am. J. Sci.* **260** (1962) 230.
8. Dunitz, J. D. and Orgel, L. E. *Advan. Inorg. Chem.* **2** (1960) 15.
9. Moore, T. E., Ellis, M. and Selwood, P. W. *J. Am. Chem. Soc.* **72** (1950) 856.
10. Graselly, G. and Klivény, E. *Acta Univ. Szeged. Acta Mineral. Petrog.* **9** (1965) 15.
11. Brenet, J. P. *Silicates Ind.* **4** (1960) 1.
12. Hahn, W. C., Jr. and Muan, A. *Am. J. Sci.* **258** (1960) 66.
13. Otto, E. M. *J. Electrochem. Soc.* **111** (1964) 88.
14. Norrestam, R. *To be published*.
15. Geller, S., Cape, J. A., Grant, R. W. and Espinosa, G. P. *Physics Letters* **24 A** (1967) 369.
16. Furnas, T. C., Jr. *Single Crystal Orienter Instruction Manual*, General Electric Co., Milwaukee 1956.
17. *International Tables for X-Ray Crystallography*. Birmingham 1962.
18. IUCr *World List of Crystallographic Computer Programs*, 2nd Ed.
19. Watson, R. E. and Freeman, A. J. *Acta Cryst.* **14** (1961) 29.
20. Suzuki, T. *Acta Cryst.* **13** (1960) 279.
21. Åsbrink, S. and Kihlberg, L. *Acta Chem. Scand.* **18** (1964) 1571.
22. Zachariasen, W. H. *Acta Cryst.* **16** (1963) 1141.
23. Åsbrink, S. *To be published*.

Received July 7, 1967.