dicular respectively to O(2^{viii})–O(2^{vi}). The thermal motion of the O atoms, especially of O(2), is nearly isotropic. The assumption of a preferred expansion of the thermal vibration ellipsoids of the Te atoms in the directions of the largest main axes by heat treatment may explain the stronger temperature dependence of the *c* axis as compared with the *a* axis.

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Structures of α-Mn_2O_3, $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ and $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$ and Relation to Magnetic Ordering

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The crystal structures of α-Mn_2O_3 and of $(Mn_{1-x}Fe_x)_2O_3$, $x=0\cdot017$ and 0·63 have been refined by least-squares calculations from three-dimensional X-ray diffraction data obtained with a Buerger–Supper–Pace–Picker diffractometer. At 25°C, crystals of α-Mn_2O_3 belong to space group *Pcab* (D_{2h}^{15}) with $a=9\cdot4157$ (3), $b=9\cdot4233$ (3), $c=9\cdot4047$ (3) Å; $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ and $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$ belong to *Ia*3 (T_h^7) with lattice constants 9·4146 (1) and 9·4126 (3) Å respectively. Interatomic distances and angles in $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ are equal to the analogous average distances and angles in α-Mn_2O_3. There appears to be significantly less distortion of the oxygen polyhedra about the 24(*d*) sites in $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$ than in $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$. Evidence is presented in support of the suggestion that the antiferromagnetic ordering temperatures depend on the allowed distortion of the Mn^{3+} ion surroundings. The results on α-Mn_2O_3 differ in minor respects from those of Norrestam (*Acta Chem. Scand.* (1967). **21**, 2871].

Introduction

This work was undertaken to gain further insight into the crystallographic and magnetic behavior of what appears to be a unique system, $(Mn_{1-x}Fe_x)_2O_3$. Early investigators (Zachariasen, 1928; Pauling & Shappell, 1930) believed α-Mn_2O_3 to be cubic and to have the same crystal structure as the mineral bixbyite ($x\simeq0\cdot5$). This conclusion was drawn on the basis of X-ray powder diffraction photography with Fe $K\alpha$ radiation. Our own work indicates that the deviation from cubic symmetry in such photographs is barely detectable, and perhaps only if one already knows that the Mn_2O_3 is not cubic. Further, less than one cation % Fe^{3+} impurity would make the compound cubic at room temperature (Grant, Geller, Cape & Espinosa, 1968).

Some structural work on α-Mn_2O_3 has also been done with neutrons both at room temperature (Fert, 1962;* Hase, 1963) and at very low temperature (Cable, Wilkinson, Wollan & Koehler, 1957). No deviation from cubic symmetry was noted by these investigators but the magnetic structure at low temperatures appeared to be very complex.

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* In a previous paper (Geller, Romo & Remeika, 1967) we pointed out that Fert's interatomic distances for Mn_2O_3 could not be correct. Fert's parameter values agree well with those found for $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$. Thus it appears that he calculated the distances for Mn_2O_3 incorrectly.

At room temperature, the distortion of α-Mn_2O_3 from cubic symmetry is observable in a powder photograph taken with Cr $K\alpha$ radiation. We reported (Geller, Cape, Grant & Espinosa, 1967) that the maximum symmetry the phase could have was orthorhombic. Not long after this report, single crystals of α-Mn_2O_3 were grown by Espinosa and the crystals were indeed found to be orthorhombic, space group *Pcab* (Geller, Grant, Cape & Espinosa, 1968). Norrestam (1967) describes a method whereby he obtained a single crystal of α-Mn_2O_3 by appropriate annealing of α-Mn_2O_3 powder. He had difficulty with twinning, but did finally find a crystal in which it was negligible. Although several of the crystals, of α-Mn_2O_3 and $(Mn_{1-x}Fe_x)_2O_3$, grown by Espinosa were examined with single-crystal X-ray photography, no twinning was observed. Norrestam (1967) has reported the structure of α-Mn_2O_3 and except for minor discrepancies to be discussed later. the results reported here confirm his.

The $(Mn_{1-x}Fe_x)_2O_3$ system has been studied to various extents by several workers (Zachariasen, 1928; Pauling & Shappell, 1930; Wretblad, 1930; Montoro, 1940; Mason, 1943; Dachs, 1956; Hase & Meisel, 1966; Hase, Kleinstück & Schulze, 1967; Hase, Brückner, Tobisch, Ulrich & Wegerer, 1969;* Grant *et al.*, 1968). Until recently, specimens were prepared by solid state reaction and structural investigations were made on powders. The mineral bixbyite has also been studied (see several of preceding references), but in this case, also, the structural investigations were made on powders. Bixbyite is cubic, as all investigators agree, and belongs to space group *Ia*3.

Initially our susceptibility and Mössbauer spectroscopic studies (Geller, Grant, Cape & Espinosa, 1967) were made on powder specimens prepared by solid state reaction. These studies produced some anomalies which were explained when homogeneous crystals were obtained (Grant *et al.*, 1968). Crystals have been grown by Espinosa, with compositions ranging from 0 to 63 cation per cent Fe^{3+}.* These enabled us to determine the phase diagram, including magnetic phases of the system (Grant *et al.*, 1968).

Experimental

All the crystals used in this investigation were grown by Espinosa (1970) by a flux method. The three crystals studied had $x=0{\cdot}00$, $0{\cdot}017$ and $0{\cdot}63$, the second and third compositions having been ascertained by chemical analysis. The crystals were ground into spheres (Bond, 1951) of radius 0·16, 0·10, and 0·11 mm respectively. Lattice constants of these specimens were determined with a Bond (1960) spectrometer. Crystal data for the specimens are given in Table 1.

The intensity data were collected with a Buerger–Supper–Pace–Picker automatic diffractometer; Mo $K\alpha$ radiation and balanced Zr and Y filters were used. In all cases, the data collected were those included within $2\theta=60°$. For the α-Mn_2O_3, the b axis was the rotation axis and all the data within the hemisphere (and $2\theta \le 60°$) were collected. For the two cubic iron-containing specimens, intensities of only independent reflections were collected.

The continuous scan mode was used with $1{\cdot}0°\ \text{min}^{-1}$ scan rate and scan interval of 2° or more. Background counts were taken at the beginning and end of the scan interval at $\frac{1}{4}$ the scan time of each reflection.

Relative $|F_o|^2$ were obtained by application of the Lorentz–polarization–Tunell and absorption factors (Bond, 1959) to the intensities. For α-Mn_2O_3, the relative $|F_o|^2$ were averaged, from which 1209 independent $|F_o|$ were obtained. A total of 207 independent inten-

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* We find no experimental support of the contention by these authors that for $0{\cdot}01 < x \le 0{\cdot}38$ in $(Mn_{1-x}Fe_x)_2O_3$, the space group is $I2_13$ instead of *Ia*3.

* Earlier, crystals of $(Mn_{0\cdot5}Fe_{0\cdot5})_2O_3$ had been grown by Banks & Kostiner (1966) by a very different technique.

Table 1. *Crystal data*

	Mn_2O_3	$(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$	$(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$
Most probable space group	*Pcab** (D_{2h}^{15})	*Ia*3 (T_h^7)	*Ia*3 (T_h^7)
Lattice constants (Å)	$a=9{\cdot}4157$ (3) $b=9{\cdot}4233$ (3) $c=9{\cdot}4047$ (3)	$a=9{\cdot}4146$ (1)	$a=9{\cdot}4126$ (3)
Unit-cell volume (Å^3)	834·45	834·46	833·93
Formula weight	157·87	157·91	159·02
Unit-cell contains	32 Mn^{3+} 48 O^{2-}	31·46 Mn^{3+} 0·54 Fe^{3+} 48 O^{2-}	11·84 Mn^{3+} 20·16 Fe^{3+} 48 O^{2-}
Calculated density (g.cm^{-3})	5·025	5·026	5·065
μ, Mo $K\alpha$ (cm^{-1})	119·45	119·76	131·64
Systematic absences	$h0l$ with $h\ne 2n$ $hk0$ with $k\ne 2n$ $0kl$ with $l\ne 2n$	hkl with $h+k+l\ne 2n$ $0kl$ with $k,l\ne 2n$ ($hk0$ with $h,k\ne 2n$ $h0l$ with $h,l\ne 2n$)	

* This space group designation adheres to the convention $c<a<b$. See also last section of *Discussion.*

Table 2. *Positional and thermal parameters* (*standard errors*)

				$10^5\times$					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
α-Mn_2O_3*									
Mn(1)	0	0	0	96 (12)	98 (12)	90 (12)	4 (3)	22 (2)	4 (1)
(2)	0	0	½	127 (12)	127 (12)	100 (12)	12 (7)	12 (7)	9 (7)
(3)	0·28479 (10)	0·25253 (5)	−0·00590 (5)	134 (11)	156 (10)	206 (10)	−5 (3)	19 (3)	−60 (6)
(4)	0·00462 (5)	0·28507 (10)	0·24564 (5)	196 (10)	145 (11)	157 (10)	−7 (3)	−66 (6)	2 (3)
(5)	0·25301 (5)	0·00130 (4)	0·28533 (10)	161 (10)	240 (11)	109 (10)	−74 (6)	−4 (3)	0 (3)
O(6)	0·13299 (32)	−0·08466 (35)	0·15030 (33)	181 (29)	251 (32)	130 (30)	−47 (24)	−29 (25)	−54 (23)
(7)	0·14435 (33)	0·12989 (34)	−0·08507 (35)	142 (29)	250 (32)	202 (32)	−20 (26)	−39 (23)	−49 (23)
(8)	−0·08038 (35)	0·14693 (33)	0·12412 (31)	198 (30)	128 (28)	197 (30)	−1 (22)	−57 (22)	−33 (24)
(9)	−0·37447 (31)	0·41757 (34)	−0·35569 (31)	180 (29)	236 (31)	73 (27)	−83 (23)	−41 (24)	−19 (22)
(10)	−0·35081 (32)	−0·37238 (33)	0·41947 (35)	129 (29)	237 (31)	183 (31)	24 (25)	7 (23)	−99 (23)
(11)	0·41306 (34)	−0·35285 (33)	−0·36571 (33)	148 (30)	130 (28)	249 (31)	−7 (22)	−62 (22)	8 (24)
$(Mn_{0.983}Fe_{0.017})_2O_3$									
M†	0	0	0	89 (8)	$=\beta_{11}$	$=\beta_{11}$	12 (4)	$=\beta_{12}$	$=\beta_{12}$
M	0·28508 (9)	0	¼	109 (10)	229 (9)	157 (9)	0	0	78 (4)
O	0·12913 (19)	0·14708 (18)	−0·08347 (22)	247 (19)	136 (18)	202 (20)	18 (16)	−131 (13)	−12 (15)
$(Mn_{0.37}Fe_{0.63})_2O_3$									
M	0	0	0	127 (10)	$=\beta_{11}$	$=\beta_{11}$	18 (5)	$=\beta_{12}$	$=\beta_{12}$
M	0·28473 (12)	0	¼	172 (13)	179 (11)	160 (11)	0	0	−36 (6)
O	0·13527 (26)	0·13950 (24)	−0·08830 (31)	183 (24)	124 (22)	270 (26)	−73 (19)	−19 (19)	50 (21)

* The atom numbers are the same as those of Norrestam (1967). See also last section of *Discussion.*
† M designates average cation.

sities was obtained from each of the two iron-containing specimens.

Refinement of the structure

In the refinement calculations, the Busing, Martin & Levy (1962) least-squares program modified by Ibers, Hamilton, Johnson, Ellison & Levy to include the imaginary part of the anomalous dispersion correction was used. Atomic form factors used were those of Cromer & Waber (1965) for Mn^{3+} and Fe^{3+} and those of Tokonami (1965) for O^{2-}. Both the real and imaginary parts of the anomalous dispersion corrections (Cromer, 1965) for the cations were used. For $(Mn_{0.983}Fe_{0.017})_2O_3$, the changes in atomic form factors from those of Mn_2O_3 were neglected. For $(Mn_{0.37}Fe_{0.63})_2O_3$, the distribution of Mn^{3+} and Fe^{3+} ions on the two sites was assumed to be random even though it is known (Banks, Kostiner & Wertheim, 1966; Grant *et al.*, 1968) not to be. However, the ionic distribution and the closeness of atomic form factor values for Mn^{3+} and Fe^{3+} for the same $\sin\theta/\lambda$ value are such that no attempt was made to refine multipliers.

The structure of $(Mn_{0.983}Fe_{0.017})_2O_3$ was refined starting with equal weights and isotropic thermal parameters. Structure amplitudes greater than 250 and a few unobserved reflections were given extremely low weights essentially removing these from the refinement. After 3 cycles, anisotropic thermal parameters were introduced and the discrepancy factor came rapidly to 0·02 excluding a few very high and a few unobserved structure amplitudes.

The thermal parameters obtained from the refinement of $(Mn_{0.983}Fe_{0.017})_2O_3$ were then applied to α-Mn_2O_3 according to the symmetry of the latter. The positional parameters were started at Norrestam's (1967) results. Eleven large structure amplitudes were given very low weights, as were also 41 low structure amplitudes which appeared, after one iteration, to have been observed larger than they should have been, probably because of radiation streaks not adequately compensated by the Y filter. (These amplitudes are also designated by an asterisk in Table 2.) All other intensities were given $\sigma=0{\cdot}046|F|$ except those with $|F|\le 20{\cdot}0$ which were all given $\sigma=0{\cdot}9$. Three least-squares cycles, in which all parameters (a total of 94 including one scale factor) were allowed to vary, brought convergence. The discrepancy factor excluding the 52 low-weight amplitudes is 0·034. Final values of the parameters are given in Table 2. A listing of observed and calculated structure may be obtained from the author upon request.

Starting parameters for $(Mn_{0.37}Fe_{0.63})_2O_3$ were those from the results of the refinement of $(Mn_{0.983}Fe_{0.017})_2O_3$. At first, equal weights were used except that several large amplitudes (indicated by asterisk in Table 3) and unobserved reflections were given low weights. Convergence was very rapid. Final cycles of least-squares calculations were run on both cubic cases with $\sigma=0{\cdot}046|F|$ for all except those with $|F|\le 20$, which in both cases were given $\sigma=1\cdot0$. These weighting schemes gave for estimated standard errors of an observation (including all amplitudes) 1·36, 0·90 and 1·17 for α-Mn_2O_3, $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ and $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$ respectively. Discrepancy factors for both $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ and $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$ are 0·027. Final parameter values and a comparison of calculated with observed amplitudes for these are given in Tables 2 and 3 respectively.

Table 3. *Comparison of calculated and observed amplitudes*, $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ *and* $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$.

$l = 0$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0	2	42	39	35	35
2	2	14	14	13	14
0	4	*277	322	315	325
4	2	43	44	47	50
2	4	45	41	54	51
4	4	*385	521	480	555
0	6	87	85	94	91
6	2	104	103	95	97
2	6	52	54	59	60
6	4	134	139	128	132
4	6	46	43	50	50
0	8	*272	382	329	333
8	2	92	94	90	92
2	8	145	149	132	136
6	6	73	21	20	23
8	4	180	190	178	182
4	8	182	192	179	183
0	10	98	99	98	101
8	6	18	17	40	39
6	8	112	115	128	132
10	2	107	108	102	105
2	10	104	106	113	115
10	4	136	142	143	148
4	10	108	110	97	101
8	8	102	100	113	118
10	6	84	87	74	75
6	10	33	35	36	35
0	12	125	128	125	125
12	2	89	92	106	105
2	12	112	115	111	114
12	4	90	91	104	109
4	12	85	87	103	107
10	8	170	174	159	163
8	10	16	17	23	25

$l = 1$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	2	94	92	96	92
3	2	43	38	26	22
2	3	27	31	25	26
1	4	50	46	71	68
4	3	127	133	133	132
3	4	131	135	125	124
5	2	78	77	83	82
2	5	63	62	70	67

$l = 1$ (Cont.)

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	6	121	123	125	126
5	4	135	141	128	135
4	5	128	132	113	116
6	3	133	133	133	134
3	6	118	117	121	122
7	2	29	31	55	55
2	7	118	118	120	121
6	5	73	72	78	78
5	6	65	64	66	64
1	8	132	134	122	123
7	4	68	68	72	69
4	7	59	60	62	62
8	3	69	70	72	73
3	8	67	67	79	76
9	2	12	13	10	11
2	9	34	33	31	32
7	6	81	82	75	75
6	7	53	51	47	48
8	5	54	55	63	63
5	8	47	45	45	46
9	4	33	32	32	33
4	9	46	48	56	57
1	10	54	53	48	48
10	3	65	63	63	62
3	10	53	53	59	58
8	7	58	59	67	67
7	8	73	73	70	71
9	6	94	94	98	95
6	9	65	66	69	69
11	2	56	54	36	36
2	11	11	11	19	17
10	5	62	63	66	66
5	10	80	79	80	80
11	4	40	40	45	46
4	11	42	43	50	50
1	12	20	20	19	19
9	8	90	91	92	94
8	9	72	72	68	67
10	7	53	54	58	57
7	10	54	54	51	53
12	3	26	24	28	26
3	12	38	38	32	31
11	6	44	46	53	55
6	11	73	74	82	83
12	5	44	44	43	42
5	12	46	44	51	50
13	2	37	35	39	36
2	13	<11	11	22	19

$l = 2$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
2	2	*401	575	490	594
3	3	152	153	150	154
2	4	64	60	60	61
4	4	34	31	36	27
5	3	33	33	49	51
3	5	60	59	68	68
2	6	*294	340	333	353
5	5	36	34	28	22
6	4	35	36	40	41
4	6	92	91	92	93
7	3	32	30	29	30
3	7	30	27	18	16
2	8	103	103	103	104
6	6	200	216	219	224
7	5	9	7	< 8	3
5	7	53	51	37	38
8	4	68	68	67	69
4	8	55	56	66	66
9	3	38	37	37	36
3	9	40	41	38	35
7	7	57	57	63	62
8	6	138	148	147	146
6	8	53	53	48	51
2	10	155	159	165	166
9	5	14	14	33	32
5	9	40	40	52	52
10	4	62	64	65	65
4	10	142	147	138	138
8	8	24	22	23	15
11	3	65	62	70	73
3	11	<10	8	25	22
9	7	21	20	25	24
7	9	32	30	39	41
10	6	92	93	100	97
6	10	93	94	96	97
11	5	47	45	51	52
5	11	12	8	21	21
2	12	113	116	109	115
12	4	116	116	96	102
4	12	73	74	71	71
9	9	41	39	23	24
10	8	<11	9	21	19
8	10	136	141	136	140
11	7	<11	10	<11	3
7	11	33	34	29	29

$l = 3$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
3	4	86	86	88	89
5	4	49	48	51	50
4	5	59	59	72	72
3	6	63	64	65	67
6	5	91	94	92	91
5	6	104	103	96	97
7	4	61	61	68	68
4	7	60	59	66	66
3	8	86	84	82	83
7	6	92	94	94	96
6	7	122	122	117	121
8	5	95	95	85	86
5	8	93	93	99	102
9	4	74	74	81	81
4	9	62	61	60	58
3	10	79	78	68	70
8	7	74	74	74	73
7	8	78	79	72	72
9	6	37	37	48	45
6	9	42	44	56	56
10	5	41	41	45	45
5	10	26	25	33	33
11	4	60	60	50	50
4	11	43	42	45	46
9	8	37	38	33	32
8	9	55	53	56	57
10	7	35	37	36	35
7	10	42	41	43	42
3	12	36	33	34	35
11	6	65	65	60	59
6	11	33	32	27	26

$l = 4$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
4	4	229	256	240	249
5	5	45	41	56	51
4	6	60	59	57	60
6	6	61	59	53	56
7	5	67	66	73	78
5	7	62	61	60	62
4	8	160	168	181	190
7	7	67	68	58	59
8	6	< 9	4	15	11
6	8	138	142	125	132
9	5	67	65	60	60

$l = 4$ (Cont.)

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
5	9	75	76	73	73
4	10	98	99	96	100
8	8	90	90	82	82
9	7	42	43	45	46
7	9	36	35	28	30
10	6	58	57	56	55
6	10	31	30	42	39
11	5	31	31	31	30
5	11	43	42	42	42

$l = 5$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
5	6	98	98	102	104
7	6	56	58	65	69
6	7	66	66	77	78
5	8	102	104	95	99
8	7	50	51	46	47
7	8	48	49	56	55
9	6	48	49	40	39
6	9	57	58	54	55
5	10	35	34	28	28
9	8	36	36	34	33
8	9	47	49	44	50
10	7	61	60	50	51
7	10	40	39	42	42

$l = 6$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
6	6	120	119	121	121
7	7	47	46	44	45
6	8	62	63	57	59
8	8	32	32	30	28
9	7	52	51	53	54
7	9	56	55	54	51
6	10	67	63	67	67

$l = 7$

		$0.017Fe^{3+}$		$0.63Fe^{3+}$	
h	k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
7	8	41	41	46	48

Interionic distances and angles

Interionic distances and angles and their estimated standard errors were calculated with the Busing, Martin & Levy (1964) computer program *ORFFE*. These are shown in Tables 4 and 5. The limits of error in the cation–oxygen distances are 0·006–0·009 Å; in O–O distances, 0·009–0·018 Å, and in oxygen–cation–oxygen and cation–oxygen–cation angles, 0·3–0·6°.

Discussion

Relationship between the cubic and orthorhombic structures

In the case of the cubic structure alone there are two descriptions with the equipoints of *Ia*3 that give indistinguishable structures. The description usually given for the bixbyite structure has cations in 8(*b*) and 24(*d*) and oxygen ions in 48(*e*), the general positions. For clarity we shall write the representative coordinates of each of the atoms for $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ in this description:

$$(1)\qquad \begin{array}{ll} \mathrm{Mn}(b) & \frac{1}{4},\frac{1}{4},\frac{1}{4} \\ \mathrm{Mn}(d) & -0\cdot0351,0,\frac{1}{4} \\ \mathrm{O} & 0\cdot3791,0\cdot1665,0\cdot3971 \end{array}$$

Translating by $\frac{\bar{1}}{4}\,\frac{\bar{1}}{4}\,\frac{\bar{1}}{4}$, we obtain

$$(2)\qquad \begin{array}{ll} \mathrm{Mn} & 0,0,0 \\ \mathrm{Mn} & -0\cdot2851,\frac{\bar{1}}{4},0 \\ \mathrm{O} & 0\cdot1291,-0\cdot0835,0\cdot1471 \end{array}$$

Table 4. *Interionic distances in* Å *and angles in degrees*

(*a*) $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$, (*b*) $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$, (*c*) analogous average from α-Mn_2O_3.

	Polyhedron about cation in 8(*a*)			Subtended angle		
	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)
(Mn, Fe)–O(6)	2·009 (2)	2·003 (2)	2·002 (3)			
O–O(6)	2·668 (4)	2·703 (3)	2·704 (4)	83·2 (1)	84·9 (1)	84·9 (1)
O–O(6)	3·005 (4)	2·957 (4)	2·957 (5)	96·8 (1)	95·1 (1)	95·1 (1)
	Polyhedron about cation in 24(*d*)					
(Mn, Fe)–O(2)	2·147 (3)	2·242 (2)	2·243 (3)			
(Mn, Fe)–O(2)	1·930 (3)	1·898 (2)	1·898 (3)			
(Mn, Fe)–O(2)	2·033 (3)	1·987 (2)	1·988 (3)			
O–O(2)	2·600 (4)	2·578 (3)	2·580 (5)	76·9 (1)	74·9 (1)	74·9 (1)
O–O(2)	2·600 (4)	2·578 (3)	2·580 (5)	82·0 (1)	83·1 (1)	83·2 (1)
O–O(2)	2·668 (4)	2·703 (3)	2·703 (3)	79·3 (1)	79·2 (1)	79·3 (1)
O–O(2)	3·391 (4)	3·481 (3)	3·483 (4)	112·4 (1)	114·2 (1)	114·3 (1)
O–O(2)	3·048 (3)	3·055 (2)	3·055 (5)	96·6 (1)	94·8 (1)	94·7 (1)
O–O	2·726 (6)	2·765 (4)	2·766 (5)	89·8 (2)	93·6 (1)	93·6 (2)
O–O	3·288 (5)	3·109 (4)	3·109 (5)	108·0 (2)	103·0 (1)	102·9 (2)
	Cation–oxygen–cation angles					
d–O–*a*(2)	96·7 (1)	93·8 (1)	93·8 (1)			
(2)	129·7 (2)	132·4 (1)	132·3 (2)			
(2)	100·4 (1)	102·1 (1)	102·1 (1)			
d–O–*d*(4)	122·8 (1)	119·8 (1)	119·7 (2)			
(4)	104·0 (1)	106·9 (1)	106·9 (1)			
(4)	96·7 (1)	94·9 (1)	94·9 (1)			

Notes: (1) Standard errors in parentheses apply to the last digits.
(2) There are six of each *a*–O–*d* angle involved in the polyhedron about the ions in the (*a*) sites.

However, this arrangement is not compatible with the *Ia*3 space group equipoints; to make it so, *y* and *z* must be interchanged, thus

$$
(3)\qquad \begin{array}{ll} \mathrm{Mn}(a) & 0,0,0 \\ \mathrm{Mn}(d) & -0{\cdot}2851,0,\tfrac{\bar{1}}{4} \\ & 0{\cdot}1291,0{\cdot}1471,-0{\cdot}0835 \end{array}
$$

The two sets of parameters, (1) and (3), give exactly the same values of structure amplitude, but there must be an interchange of axes and therefore indices, *e.g.* $F_{hkl}(1)=F_{khl}(3)$.

There are two ways in which sets (1) and (3) may go into the orthorhombic structure. One is by way of set (2), that is, the translation $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ from set (1). This is the description given by the parameters for α-Mn_2O_3 in Table 2 in space group *Pcab*. Set (3) is equivalent to this because an interchange of *y* and *z* coordinates and of *b* and *c* simply alters the space group designation to the equivalent *Pbca*, used by Norrestam (1967) (see also last section of *Discussion*).

There is another, quite different way in which the structure *might* transform from cubic to orthorhombic. The set (1) might go directly into the orthorhombic structure without translation, *i.e.* the Mn^{3+} ions in 8(*b*) might go into a set of general positions in the orthorhombic space group. This case *is* distinguishable from the above. Thus while our 'guess' (Grant *et al.*, 1968) regarding distinguishing these two structures was not correct, the possibility that the 25 °K transformation of α-Mn_2O_3 might involve a shift in symmetry center, *i.e.* to the structure with all atoms in general positions (Grant *et al.*, 1968), is a valid suggestion. It should be recalled that the *powder* data at 6·5 °K showed no noticeable change in structure, even though the transformation at 25 °K appears to be first order (Grant *et al.*, 1968; Geller & Espinosa, 1970).

Phase transition from orthorhombic to cubic

There are two independent pieces of experimental evidence which indicate that the orthorhombic-to-cubic transition which occurs at 302 °K is higher than first order. X-ray powder diffraction photographs of α-Mn_2O_3 were taken in the temperature range 81 to 702 °K. No discontinuity in lattice constant or volume was observed. The plot of lattice constant *vs.* temperature in the important range is given in a previous paper (Geller & Espinosa, 1970). Mössbauer effect spectroscopic measurements were made on specimens $(Mn_{0{\cdot}972}Fe_{0{\cdot}028})_2O_3$ and $(Mn_{0{\cdot}94}Fe_{0{\cdot}06})_2O_3$ which have orthorhombic-to-cubic transitions at 260 and 165°K respectively. For each, the quadrupole splittings of Fe^{3+} ions in the 8(*b*)* and 24(*d*) sites increased markedly but continuously with decreasing temperature below the transition temperatures (see Fig. 5 of Grant *et al.*, 1968). No discontinuities occurred in either the isomer, shifts or absorption line widths (see Figs, 6 and 7, respectively, of Grant *et al.*, 1968). In view of the observed nature of this orthorhombic → cubic transformation of the Mn_2O_3 it was pleasantly surprising that in no case did we find the crystals to be twinned.

Comparison of the three structures

Among sesquioxides of the trivalent ions of Ti, V, Cr, Mn, Fe and Ga, Mn_2O_3 is the only one that does not have a corundum-type structure. This is not a result of ionic size because Mn^{3+} is slightly smaller than

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* 8(*a*) in the description of Table 2.

Table 5. *Interionic distances in* Å *and angles in degrees*, α-Mn_2O_3

Polyhedron about atom 1			Polyhedron about atom 3			Polyhedron about atom 4			Polyhedron about atom 5		
Atoms		∠O–Mn–O	Atoms		∠O–Mn–O	Atoms		∠O–Mn–O	Atoms		∠O–Mn–O
1—6 (2)	2·050		3—9	2·297		4—7	2·268		5—8	2·267	
1—7 (2)	1·996		3—6	2·190		4-10	2·223		5-11	2·215	
1—8 (2)	1·963		3—8	2·001		4—9	1·992		5-10	2·006	
6—8 (2)	2·693	84·3	3-11	1·976		4—6	1·981		5—7	1·972	
7—8 (2)	2·702	86·1	3—7	1·907		4—8	1·908		5—9	1·911	
6—7 (2)	2·716	84·3	3-10	1·889		4-11	1·888		5—6	1·883	
7—8 (2)	2·894	93·9	6-11	2·569	75·9	6-10	2·568	75·1	7-11	2·577	75·7
6—8 (2)	2·977	95·7	8—9	2·593	73·8	7—9	2·590	74·6	8-10	2·585	74·2
6—7 (2)	3·000	95·7	7-11	2·577	83·1	6-11	2·569	83·1	6-10	2·568	82·6
			8-10	2·585	83·3	8—9	2·593	83·3	7—9	2·590	83·7
Polyhedron about atom 2			6—8	2·693	79·8	9-10	2·689	79·1	10-11	2·703	79·5
2-11 (2)	2·047		9-11	2·715	78·5	6—7	2·716	79·1	7—8	2·702	78·9
2-10 (2)	1·998		6—7	3·465	115·3	10-11	3·470	114·9	9-11	3·469	114·3
2—9 (2)	1·960		9-10	3·511	113·6	7—8	3·502	113·7	6—8	3·483	113·8
9-10 (2)	2·689	85·6	6-10	3·014	95·0	8-10	3·058	95·2	6-11	3·011	94·2
10-11 (2)	2·703	83·8	7—9	3·090	94·1	7-11	3·061	94·4	8—9	3·098	95·3
9-11 (2)	2·715	85·3	7-10	2·766	93·5	8-11	2·765	93·5	6—9	2·766	93·6
9-10 (2)	2·905	94·4	8-11	3·111	102·9	6—9	3·108	102·9	7-10	3·110	102·8
9-11 (2)	2·948	94·7									
10-11 (2)	3·010	96·2									

Notes: (1) For atom identification, see Tables 2 and 4.
(2) Estimated standard errors are: 0·002 Å for a Mn–O distance, 0·004–0·005 Å for an O–O distance and 0·1–0·2° for an angle.

Fe^{3+} (Geller, 1957), smaller than both Ti^{3+} and V^{3+} and larger than Cr^{3+} and Ga^{3+} (Geller, 1957; see also Shannon & Prewitt, 1969). It is very likely a result of the large Jahn–Teller distortion (Dunitz & Orgel, 1957) associated with Mn^{3+} (Geller *et al.*, 1967). It is unlikely that any other oxide (*i.e.* not a solid solution with Mn_2O_3) will ever be found to have the orthorhombic structure of α-Mn_2O_3. The cubic strucure allows less distortion than the orthorhombic (see Tables 2, 4 and 5).

At a substitution of about 0·75 cation % Fe^{3+} for Mn^{3+}, the structure becomes cubic at room temperature (Grant *et al.*, 1968). However, the structure of $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ was refined because of the immediate availability of a spherical single crystal from previous experiments. The additional one cation % Fe^{3+} does not make a measurable structural difference as indicated by the results shown in Table 4: in every case of distance and angle, the average from the α-Mn_2O_3 differs by one standard deviation or much less from the analogous distance or angle in

$$(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3 .$$

In the cubic structure the Mn(*a*)–O distances (Table 4) are all equal, 2·003 Å. while the analogous (six nonequivalent) Mn–O distances (Table 5) in the orthorhombic structure range from 1·960–2·050 Å. In the cubic structure the Mn(*d*)–O distances are of three lengths ranging from 1·987–2·242 Å, while in the orthorhombic structure the analogous (18 nonequivalent) distances range from 1·883–2·297 Å. It should be kept in mind that if we accept the results on $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ to represent those just above the transition of α-Mn_2O_3 at 302 °K, these differences in the range of distances occur for a difference of only 7 °K. One is then led to wonder why, if the Mn^{3+} prefers the greater number of degrees of freedom, it transforms to the cubic structure at such a low temperature. There is the possibility that in the cubic structure and especially in the high symmetry *a* (or *b*) sites, there is electronic disorder of some sort. The disorder could be dynamic (Gyorgy, LeCraw & Sturge, 1966; Iida, Mizushima, Yamada & Iizuka, 1968) or static – that is, all the Mn(*a*)–O distances may not actually be equal but so distributed as to give a statistically cubic crystal. Some disorder may also exist about the cations in the orthorhombic structure decreasing with decreasing temperature.

The distortion in the orthorhombic structure increases considerably with decreasing temperature as is established from the measurements of quadrupole splittings (Grant *et al.*, 1968). These splittings increase continuously down to liquid N_2 temperature, but there is little, if any, tendency for the lines in the powder spectra to resolve into sets of three and two. Thus the increase in distortion with decreasing temperature is considerably larger than the differences in distortion caused by non-equivalent ions originating from the same set of equipoints of the cubic structure. Also the lattice constants of Mn_2O_3 itself reach near constancy at about 150° K; thus the lattice constants do not in this case give an indication of changes occurring in the structure, but there is no question that the quadrupole splittings do (see for example, Grant, 1969; Colville, 1970).

Of sesquioxides with the *C*-type structure, refinements, with accuracy comparable with the present ones, were done on Sc_2O_3 (Geller, Romo & Remeika, 1967, 1968; Norrestam, 1968), In_2O_3 (Marezio, 1966) and Y_2O_3 (Paton & Maslen, 1965; O'Connor & Valentine, 1969*). For Sc_2O_3 and In_2O_3, the average *d*-site cation–oxygen distance is equal (± 0·01 Å) to the *b*-site cation–oxygen distance; for Y_2O_3, Paton & Maslen (1965) give for the average Y(*d*)–O distance a value 0·04 Å greater than Y(*b*)–O, while O'Connor & Valentine (1969) find that they are equal. In α-Mn_2O_3 the average of the Mn(*c*)–O distances is 0·041 Å greater than the average of the Mn(*a*)–O and Mn(*b*)–O distances. In $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$, the difference between analogous distances is 0·039 Å, while the analogous difference in $(Mn_{0\cdot37}Fe_{0\cdot63})_2O_3$ decreases to 0·028 Å. There is no significant difference among the *overall* average cation–oxygen distances.

It is quite clear that saturation of the Mn_2O_3 structure with Fe^{3+} changes one of the cation–oxygen distances drastically (see Table 4). The range width of Mn–O distances is reduced from 0·344 Å in $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ to 0·217 Å in $(Mn_{0\cdot37}Fe_{0.67})_2O_3$. For Sc_2O_3 the analogous value is 0·08 Å; for In_2O_3, 0·10 Å; for Y_2O_3, 0·09 or 0·10 Å. The largest range is found in α-Mn_2O_3 itself (see Table 5), namely 0·414 Å. Thus it is evident that the Mn^{3+} ion behaves quite differently from the other cations in the *C*-type structure. Especially, these results emphasize that Mn^{3+} requires more distorted surroundings.

Magnetic aspects

Mn_2O_3 has an antiferromagnetic transition at 80 °K (King, 1954; Meisenheimer & Cook, 1959; Geller *et al.*, 1967; Grant *et al.*, 1968) and another antiferromagnetic transition at 25° K (Geller *et al.*. 1967; Grant *et al.*, 1968; Chevalier, Roult & Bertaut, 1967†); the latter appears to be first order. Replacement of Mn^{3+} by Fe^{3+} causes a reduction in all transition temperatures. The lower antiferromagnetic one decreases rapidly with Fe^{3+} substitution; at 0·75 cation % Fe^{3+}, it occurs at 19 °K and it is not observed in a specimen with 2·8 cation % Fe^{3+} substitition (Grant *et al.*, 1968). Smaller ions, however tend to raise the temperature of the lower transition (Geller & Espinosa, 1970). Because of this trend, the reordering would appear to involve some atomic displacements in accord with the aforementioned suggestion regarding this transition.

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[*] Comments made by these authors relative to interatomic distances in bixbyite are not supported by the results of the present work.

[†] The lower temperature transition was found by neutron diffraction, but the transition temperature reported is not in accord with that determined in our experiments.

As the temperature decreases below the cubic to orthorhombic transition temperature the quadrupole splittings associated with the ions in the two kinds of sites increase continuously (Grant, 1969). Thus it is probable that the room temperature structures (especially of the cubic ones which transform to the orthorhombic) can be only symptomatic of what occurs at the lower temperatures. The suggestion is that the onset of magnetic ordering is somehow associated with the amount of distortion.

There appears to be a close association of the magnetic ordering of the orthorhombic phases, $(Mn_{1-x}Fe_x)_2O_3$ $0 \leq x \leq 0{\cdot}09$, with the Jahn–Teller distortion of the Mn^{3+} ions. The substitution of Fe^{3+} for Mn^{3+} tends to reduce the distortion (see Table 4) and the magnetic ordering temperature in the orthorhombic region (Grant *et al.*, 1968). In the orthorhombic region, substitution of the diamagnetic ion Ga^{3+} for Mn^{3+} has about the same effect on the upper Néel temperature as the same amount of Fe^{3+}; there is a strong indication that above 38 cation % Ga^{3+}, well into the cubic region, there will be no further magnetic ordering (Geller & Espinosa, 1970). This is in contrast to $(Sc_{0\cdot5}Fe_{0\cdot5})_2O_3$, with the same structure, which has a magnetic ordering temperature of approximately 35°K (Geller, Williams & Sherwood, 1961*). There is only a small increase in Néel temperature in the cubic region of the $(Mn_{1-x}Fe_x)_2O_3$ system, *i.e.* from 9 to 63 cation % Fe^{3+} (Grant *et al.*, 1968).

There are no *a*–O–*a* type magnetic interactions (see Table 4) and it would therefore seem that the magnetic ordering in the *a*-type sites is tied intimately to that in the *d*-type sites. Also there are twice as many *d*–O–*d* as *d*–O–*a* interactions (Table 4). Thus it would appear that magnetic ordering could be attained with paramagnetic ions exclusively in *d*-type sites, but not with paramagnetic ions exclusively in *a*-type sites.

It has been shown (Geller & Espinosa, 1970) that the substitution of Cr^{3+} for Mn^{3+} ion in Mn_2O_3 does not have as large an effect as Fe^{3+} ion substitution on the Néel temperature. For 8 cation % Cr^{3+} substitution the upper Néel temperature, T_{N1}, is 71 °K, while it is down to 42 °K for 8 cation % Fe^{3+}; at 12 cation % Cr^{3+}, the upper Néel temperature, T_{N1}, is reduced only to 68 °K. The explanation hypothesized for this is the greater compatibility of Cr^{3+}, which has empty e_g orbitals, with Mn^{3+} which has one electron in the e_g orbitals as opposed to any ion with a filled, half-filled or completely empty *d*-shell. It appears that as a result of gaining further insight into the structures, this explanation may now be extended.

Probably because of the Cr^{3+} electronic configuration,* the range of Cr^{3+} substitution in which the structure may still be orthorhombic (at temperatures > 0 °K) is wider than for all the other substituent ions (see Geller & Espinosa, 1970). Thus as long as the structure can remain orthorhombic, the Mn^{3+} ions in the more symmetric sites can have their distorted surroundings with which the magnetic ordering must be importantly linked. There is some evidence to support such a hypothesis. An extrapolation of the line through the Néel temperatures of cubic phases, *i.e.* for $x > 0{\cdot}09$, to $x = 0$ gives a Néel temperature of ~ 26 °K (see Fig. 3 of Grant *et al.*, 1968). This implies that if pure Mn_2O_3 had the cubic structure it would have only about one-third the Néel temperature it actually has. There is also the possibility that the spins of Mn^{3+} ions in the high symmetry (*a*) sites are not ordered in the cubic antiferromagnetic phases.

Comparison of present and Norrestam's results for α-Mn_2O_3

The transformation 100|001|010 takes the Mn_2O_3 positional parameters given in Table 2 into those of Norrestam. This implies that the transformation 100|001|010 takes our axes and reflexion indices into those of Norrestam. There is agreement for the transformation of indices (obtained by comparing observed structure amplitudes) and for the transformation of our *b* to Norrestam's *c* axis, both of which equal 9·4233 Å. However, our *a* axis of 9·4157 Å transforms to his of 9·4118 Å, and our *c* axis of 9·4047 Å transforms to his of 9·4177 Å. Not only do the lengths not agree but the size order is reversed.

The reasons for these discrepancies are not known. They are not a result of the different working temperature: Norrestam's was 27·5°, ours 25° C. According to our measurements of lattice constant *versus* temperature (Geller & Espinosa, 1970), neither of the two smaller axes ever reaches 9·4177 Å below the transition temperature. Further, the average value of our axes at 25°C is 9·4146 ± 0·0003 Å, exactly equal to the lattice constant of $(Mn_{0\cdot983}Fe_{0\cdot017})_2O_3$ (see Table 1). Norrestam's average value is 9·4176 ± 0·0007 which seems much too high.

Norrestam's data covered a larger range of $\sin^2\theta$, namely to 0·6 while our data went only to $\sin^2\theta = 0{\cdot}25$; we observed many more of the faint reflections in the range covered. Although the *R* value is slightly higher than Norrestam's, the estimated standard errors in positional parameters and Mn–O distances are half his. There are some large differences in thermal parameters especially for β_{ij}, $i \neq j$.† Norrestam's σ values for these are in some cases 4 times as large as those given in

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* In the earlier paper, Geller *et al.* (1961) reported magnetic transitions at 7 ± 1 °K and 'possibly one at about 35 °K'. Recent Mössbauer effect measurements by Grant in this laboratory on a new $(Sc_{0\cdot5}Fe_{0\cdot5})_2O_3$ specimen confirm the higher temperature transition. However, susceptibility and Mössbauer measurements do not confirm the lower one.

* This can include the effect of electronic configuration on site preference.

† The Busing–Levy program refines the parameters of

$$T = \exp\left(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23}\right).$$

Norrestam's β_{ij} values contain the factor of 2. However, the differences referred to take this into account.

Table 2. Further, there is perhaps a little more reasonableness to the β values given in Table 2 of the present paper. There are some differences in positional parameters and interatomic distances, but in view of Norrestam's larger estimated standard errors, these do not appear to be statistically significant.

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