Zeitschrift für Kristallographie, Bd. 130, S. 139–147 (1969)

The crystal structure of manganese metagermanate, $MnGeO_3$*

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(Received 20 November 1968)

Auszug

Die Kristallstruktur von $MnGeO_3$ wurde auf Grund von zwei unabhängigen Meßreihen der Intensitäten von *hkl*-Interferenzen bis zum Wert $R = 0{,}08$ verfeinert. Die Gitterkonstanten sind $a = 19{,}267$ Å, $b = 9{,}248$ Å, $c = 5{,}477$ Å; $Z = 16$; Raumgruppe *Pbca*. Die Verbindung ist isotyp mit Enstatit, $MgSiO_3$. Die Ketten von GeO_4-Tetraedern werden durch Oktaeder um die Mn-Atome verbunden. Die mittleren Abstände sind: Ge—O = 1,75 Å und Mn—O = 2,21 Å.

Abstract

The crystal structure of manganese metagermanate, $MnGeO_3$, has been refined. Two independent sets of three-dimensional x-ray intensities were measured. The crystallographic data are: $a = 19.267$ Å, $b = 9.248$ Å, $c = 5.477$ Å; $Z = 16$ and space group *Pbca*. The compound is isotypic with enstatite, $MgSiO_3$. Using the positional parameters of enstatite as a starting point, the structure was refined to $R_F = 0.08$.

The essential feature of the structure is the linkage of GeO_4 tetrahedra to form single chains running parallel to the *c* axis. The chains are bound together by manganese octahedra. There are two crystallographically different chains, arranged with the vertices of alternate tetrahedra pointing in opposite directions. Average Ge—O and Mn—O distances are 1.75 Å and 2.21 Å, respectively.

Introduction

Crystal structures of pyroxene-group minerals are of great interest because they form an important group of rock-forming ferromagnesian silicates. Recent development of single-crystal counter diffractometers, coupled with high-speed electronic computers, rejuvenated interest in

* Presented at the ACA Atlanta, Georgia Meeting, January 1967.

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Table 1. *Crystal data for* $MnGeO_3$

System:	Orthorhombic
Space group:	*Pbca*
Cell parameters:	$a = 19.267 \pm .006$ Å
	$b = 9.248 \pm .003$
	$c = 5.477 \pm .002$
Number of formulae per unit cell:	$Z = 16$
Calculated density:	4.777 g/cm^3
Linear absorption coefficient for Mo$K\alpha$:	181.6 cm^{-1}

these structures among mineralogists. A good review of the present status of refinement of these minerals has been given by PREWITT and PEACOR (1964).

During the phase studies of GeO_2—$MnGeO_3$ by TAUBER, KOHN, WHINFREY and BABBAGE (1963), single crystals of $MnGeO_3$ were grown and determined to be isotypic with enstatite, $MgSiO_3$. Since no structural work had been reported on germanium analogues of the pyroxene structures, this investigation was undertaken to provide precise information for the crystal structure of $MnGeO_3$, in the hope that meaningful correlations and comparisons could be made between the isotypic germanates and silicates.

The crystallographic data of $MnGeO_3$ are shown in Table 1.

Intensity measurement

Two sets of intensities were measured independently. One set (data I) was taken with a General Electric XRD-6 diffractometer equipped with a Datex semi-automatic remote controller. The dimensions of the first crystal were $0.006 \times 0.012 \times 0.016$ cm. The stationary-crystal, stationary-counter technique was used with a pair of balanced filters. Reflections up to $2\theta = 60°$ were measured employing Mo$K\alpha$ radiation. Peak intensities were counted at a fixed time of 20 seconds. A standard reflection, 600, was measured each day throughout the experiment and the fluctuations in the intensities were found to be within 5%. Intensities were corrected for absorption, Lorentz and polarization effects, using the Los Alamos program (LARSON, CROMER and ROOF, JR., 1964).

The second set (data II) was measured with an automated Buerger diffractometer. A different crystal ($0.01 \times 0.021 \times 0.025$ cm) was selected. Details of the data collection are described elsewhere (ROBINSON and FANG, 1969).

Refinement of the structure

Since the isotypism between $MnGeO_3$ and enstatite, $MgSiO_3$, had been established, the structure refinement was initiated using LINDEMANN's (1961) coordinates for enstatite. The least-squares program used in the refinement was coded by BUSING, MARTIN and LEVY (1962). Form factors for O^{2-} were those of SUZUKI (1960) and those for Mn^{2+} and Ge^{4+} were taken from the International tables for x-ray crystallography (1962). Using data I, after six isotropic cycles, the R value for 694 observed reflections (of unit weight) dropped from 35% to 8.6%. Using data II, the R value improved from 34% to 8.0%. Anisotropic refinement was attempted, but the coefficients of all oxygen atoms failed the positive-definite test. Table 2 lists the atomic coordinates and the isotropic temperature factors obtained from data II. Data II gave an improved R value as well as smaller standard deviations. Observed and calculated structure factors (from data II) are given in Table 3. To aid in the comparison among different atomic designations used by various authors, the following tabulation is given:

Site nomenclatures

This study	BURNHAM (1967)	LINDEMANN (1961)	GHOSE (1965)
Mn(1)	M1	Mg_1	M_I
Mn(2)	M2	Mg_2	M_{II}
Ge(1)	SiB	Si_1	Si_1
Ge(2)	SiA	Si_2	Si_2
O(1)	O1-B	O_2	O_1
O(2)	O2-B	O_3	O_5
O(3)	O3-B	O_1	O_3
O(4)	O1-A	O_4	O_4
O(5)	O2-A	O_5	O_2
O(6)	O3-A	O_6	O_6

Discussion of the structure

The general feature of the structure is the linkage of GeO_4 tetrahedra through sharing of two out of four corners to form a single, continuous chain parallel to the c axis. Chains repeat at every third tetrahedron and are bound together by octahedrally coordinated Mn atoms. Thus another way of describing the structure is that it is composed of alternate layers of Ge tetrahedra and Mn octahedra.

Table 2. *Final coordinates of* $MnGeO_3$

Atom	x	y	z	B
Mn(1)	.1238(2)	.3465(4)	.3588(5)	.28(4) Å^2
Mn(2)	.3777(2)	.4819(4)	.3515(5)	.34(4)
Ge(1)	.4728(1)	.1631(3)	.2981(3)	.13(3)
Ge(2)	.2702(1)	.3438(3)	.0340(3)	.12(3)
O(1)	.0621(8)	.1575(21)	.1890(26)	.72(21)
O(2)	.0685(8)	.5161(18)	.1856(26)	.51(21)
O(3)	.4442(8)	.3098(17)	.1097(24)	.41(20)
O(4)	.1802(6)	.3356(19)	.0224(21)	.13(16)
O(5)	.1923(8)	.0083(18)	.0467(24)	.44(20)
O(6)	.3962(7)	.2787(16)	.3137(24)	.24(18)

Table 4 summarizes the bond lengths and angles, calculated by ORFFE (BUSING, MARTIN and LEVY, 1964). It is noted that the mean values for the two independent Ge(1)—O and Ge(2)—O distances are in close agreement. However, the mean value of the Ge—O (bridge) distances is 1.797 Å, appreciably longer than the mean Ge—O (unlinked) distance of 1.715 Å. This is consistent with the results reported for $CoGeO_3$ (PEACOR, 1968) where the difference is 0.06 Å, and for $NaFeGe_2O_6$ (SOLOV'EVA and BAKAKIN, 1968) where the difference is about 0.1 Å. Such a difference can be explained in terms of the d-p π bonding theory suggested by CRUICKSHANK (1961). Although his treatment is for the Si—O bond, the identical electronic configuration (of s and p suborbitals) of Si and Ge permits the same interpretation as far as their bonding characteristics are concerned. In pyroxenes (metasilicates), it is found that the Si—O (bridge) bonds tend to be about 0.05 Å longer than Si—O (unlinked) bonds, where the Si—O—Si angle is about 135°. If this angle were about 120° (oxygen atoms in ideal close packing), the calculated difference would be about 0.14 Å. Thus CRUICKSHANK interpreted the smaller actual difference to be partly due to the opening of Si—O—Si angles. A similar situation occurs in $MnGeO_3$, where the proximity to 120° (Ge—O—Ge is 126°) is reflected in the difference of 0.08 Å between the bridging and non-bridging Ge—O distances.

The O—O—O angles, which are indicative of the "straightness" of the chains, are listed in Table 4-VI. The values show different degrees of straightness of the two chains.

Table 5 shows the valency calculation in the usual way. Apparently, PAULING's classical electrostatic rule is satisfied on the average:

Table 3. *Observed and calculated structure factors*

h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
6 0 0	70	− 71	20 12 0	138	−151	21 4 1	79	73	12 13 1	62	58	9 4 2	44	− 26	11 11 2	78	73
8	166	186	24	64	− 60	22	90	− 84	15	55	157	11	38	− 33	12	142	147
10	42	− 43	2 13 0	67	66	23	79	− 71	17	54	49	12	40	− 38	15	51	− 51
12	267	−320	10	110	125	25	84	82	19	73	− 73	13	48	− 36	16	80	77
14	115	−115	22	65	− 66	2 5 1	71	− 70	22	59	− 63	14	64	− 59	17	118	−125
16	95	91	10 15 0	75	74	3	42	47	2 14 1	101	− 98	15	41	− 28	18	64	− 69
20	301	−355	14	70	72	4	69	68	3	108	−104	16	40	− 28	23	66	− 59
22	61	− 28	0 16 0	166	−177	5	91	79	4	121	−111	17	44	− 38	25	88	− 92
24	95	− 85	8	84	− 86	6	89	87	5	93	91	18	111	−108	29	77	87
26	90	102	6 17 0	130	−139	7	66	− 62	8	80	77	19	46	36	2 12 2	144	−147
28	156	−174	14	126	−138	8	71	72	13	56	58	22	97	− 92	3	87	78
30	63	59	0 18 0	60	78	13	41	35	15	74	70	23	49	43	6	57	− 51
32	109	108	4	61	69	14	102	105	16	95	96	26	69	− 64	9	79	77
34	108	113	4 1 1	103	102	15	50	− 41	17	61	− 58	27	61	56	11	79	77
4 1 0	35	32	5	140	145	16	43	39	18	67	68	1 5 2	50	− 32	18	77	70
10	211	232	6	107	103	26	63	65	8 15 1	71	− 68	2	66	− 49	22	97	96
14	237	267	7	109	−112	0 6 1	56	51	9	59	− 48	3	214	228	23	73	− 72
16	48	− 38	8	118	116	1	83	− 82	10	66	− 60	4	122	113	7 13 2	55	− 54
20	93	− 94	9	81	68	3	63	65	11	63	58	5	129	120	8	53	− 54
22	45	47	11	94	− 94	7	38	32	12	64	− 62	6	41	22	12	60	− 56
24	95	− 80	12	84	66	12	41	− 34	0 16 1	65	70	7	49	− 29	13	66	62
26	103	−105	13	81	74	1 7 1	59	51	1 0 2	109	97	8	223	246	12 15 2	68	− 73
30	76	− 81	14	95	− 86	2	62	52	2	314	−409	9	180	−180	2 16 2	94	94
34	122	−124	15	101	86	3	57	− 47	3	226	246	10	52	− 45	3	75	− 73
0 2 0	116	−111	16	79	85	4	69	58	4	112	101	11	124	115	11	63	− 71
4	214	−258	19	57	− 53	5	101	98	5	226	−250	12	220	230	3 17 2	77	78
8	47	50	26	59	− 64	6	65	59	6	138	−125	13	43	23	8	82	88
10	57	63	28	60	− 59	7	75	− 76	7	115	− 94	15	80	− 71	9	75	− 77
16	130	130	1 2 1	147	147	8	102	99	9	222	243	16	119	118	2 1 3	68	− 63
24	101	97	2	211	−247	9	121	120	11	287	334	17	171	−173	3	141	−136
4 3 0	37	27	3	211	−232	10	66	56	12	159	123	18	93	− 90	4	23	− 7
10	72	67	4	208	−235	11	107	−113	14	85	77	22	63	− 64	5	46	− 38
12	35	− 34	5	215	247	12	93	92	15	105	− 97	23	77	− 68	6	103	−100
14	60	58	6	92	− 88	13	62	61	17	135	126	25	99	− 94	7	86	− 77
0 4 0	151	−169	7	63	52	15	83	− 80	18	164	162	26	70	− 65	9	109	107
4	193	−215	8	120	117	16	57	56	20	56	33	28	86	− 81	10	113	− 95
8	111	−111	9	49	49	17	44	43	21	75	− 68	29	99	96	11	75	− 56
10	88	96	10	43	38	19	76	− 83	22	196	199	32	89	− 90	13	67	60
14	39	36	11	61	− 57	31	61	67	23	199	−200	0 6 2	39	− 14	14	64	60
16	138	142	12	57	− 46	1 8 1	80	83	24	94	− 64	1	48	31	17	114	112
20	135	135	13	86	83	2	148	−148	25	67	43	2	254	−299	18	54	− 37
24	88	88	14	76	69	3	191	−192	26	93	84	3	186	190	0 2 3	259	296
2 5 0	154	156	15	107	98	4	193	−193	31	118	−123	4	69	58	1	216	240
10	169	−175	16	169	171	5	173	175	32	94	− 97	5	128	−119	3	85	− 78
12	43	44	17	118	−100	6	84	− 77	3 1 2	133	−131	6	99	− 99	4	102	95
14	314	−363	18	142	129	7	48	36	4	64	− 63	7	54	− 41	5	81	− 70
16	45	44	19	61	41	8	140	144	5	133	−131	9	177	179	6	51	− 33
18	55	46	21	92	− 86	11	48	− 44	6	55	− 51	11	195	206	7	220	−240
22	63	− 67	22	100	92	12	58	− 47	8	217	−241	12	83	82	8	101	90
26	135	142	23	130	123	13	83	80	9	133	109	14	93	62	9	45	− 21
28	54	55	24	98	86	14	47	45	10	61	39	15	62	− 52	10	63	− 52
34	149	149	25	121	−117	15	100	99	11	129	−116	17	84	77	11	60	− 50
4 6 0	66	69	26	70	52	16	127	134	12	252	−268	18	118	118	12	87	− 78
6	51	− 49	28	74	− 72	17	93	− 84	13	103	55	19	46	41	13	146	−138
8	177	187	29	57	− 50	18	120	122	14	57	30	21	57	− 53	14	67	− 41
10	59	− 57	33	67	− 64	21	70	− 70	15	48	41	22	109	160	15	106	−101
12	184	−192	36	72	− 77	22	78	73	16	133	−129	23	159	−155	16	54	− 37
14	80	− 86	1 3 1	202	−238	23	113	116	17	159	150	24	68	− 54	19	142	140
20	265	−285	2	186	−204	24	112	107	18	90	65	26	86	80	20	144	−136
24	75	− 70	4	50	− 51	25	112	−112	22	58	59	31	92	−101	21	93	− 75
26	59	66	5	82	76	26	60	45	23	70	63	32	74	− 80	23	71	67
28	115	−121	6	150	148	28	65	− 68	24	57	46	1 7 2	59	− 58	24	59	− 56
32	86	84	7	44	35	1 9 1	103	− 96	25	53	45	2	55	− 35	27	137	141
34	92	105	8	176	−188	2	117	−109	26	56	58	3	53	− 39	28	68	− 58
2 7 0	75	77	9	232	−255	4	60	− 40	28	72	69	4	78	− 70	1 3 3	278	334
4	87	88	10	287	−318	8	114	−114	29	65	− 54	7	77	− 69	2	71	− 57
6	120	126	11	276	318	9	133	−132	32	78	74	8	142	−139	3	38	− 20
10	191	206	12	230	−244	10	155	−161	1 2 2	45	39	12	143	−147	4	63	51
14	114	111	13	78	− 67	11	152	154	2	93	85	13	77	76	5	148	−139
18	51	51	14	55	43	12	147	−152	3	40	40	16	70	− 68	6	210	215
30	71	− 78	15	93	92	13	47	− 42	4	43	42	17	56	54	7	201	211
2 8 0	56	− 57	16	54	− 42	15	61	62	5	46	− 43	21	60	58	8	53	33
4	106	−103	17	148	−153	16	46	− 44	6	119	115	22	63	57	9	41	− 26
16	79	81	18	99	− 83	17	75	− 68	7	134	−136	1 8 2	45	34	10	124	122
18	52	20	19	126	122	18	48	− 39	8	70	− 60	3	49	42	12	45	− 39
10 9 0	98	99	21	82	70	19	76	77	9	57	47	4	46	47	13	257	−283
14	75	81	22	168	176	22	93	89	10	52	41	5	58	− 44	14	204	198
16	69	− 58	24	92	91	24	74	73	11	36	− 11	6	53	28	15	127	113
0 10 0	201	−211	29	80	77	30	76	86	12	42	− 33	7	63	− 60	16	56	− 56
4	103	−107	30	112	108	31	65	− 64	13	75	− 66	13	53	− 51	19	104	− 95
8	110	−119	31	94	− 83	0 10 1	101	107	14	63	− 53	15	51	− 58	20	67	− 49
10	89	43	32	98	88	1	101	− 93	15	69	− 63	8 9 2	63	− 63	21	198	−203
12	71	50	35	66	− 63	2	78	70	16	41	− 32	12	78	− 69	22	64	25
16	62	69	0 4 1	57	53	6	51	53	17	44	− 33	13	53	48	26	77	− 79
20	145	158	1	151	−160	8	45	47	18	110	−104	14	46	47	27	60	− 54
24	64	59	2	167	183	11	49	− 34	19	79	72	2 10 2	151	150	33	152	160
28	78	57	3	104	99	12	73	− 70	22	57	− 59	3	97	− 93	34	91	− 84
2 11 0	101	94	4	106	104	14	60	− 63	27	55	52	6	87	88	0 4 3	195	−202
6	234	−244	5	153	−156	18	57	− 63	3 3 2	33	− 28	9	52	− 46	1	123	−123
8	59	− 18	6	83	79	20	60	− 63	4	45	− 43	11	63	− 63	2	47	− 26
10	91	− 98	9	65	− 60	21	51	41	5	34	30	14	49	− 46	3	146	140
14	221	−257	12	39	− 28	22	62	− 57	7	33	− 22	17	52	− 47	4	114	−105
18	53	53	13	39	− 33	6 11 1	58	61	8	45	− 37	18	88	− 90	5	51	37
20	85	93	14	83	− 81	1 12 1	68	− 68	9	36	12	22	91	− 94	7	136	127
22	63	− 59	15	42	− 32	3	58	61	0 4 2	56	− 56	23	58	61	8	49	− 36
26	114	− 23	16	107	−112	2 13 1	55	49	2	178	192	3 11 2	155	150	9	79	73
0 12 0	233	230	17	63	52	8	73	71	3	84	− 73	5	90	80	10	52	46
4	74	78	18	98	− 95	9	103	103	6	121	121	7	49	− 34	11	79	76
8	61	69	19	65	− 59	10	82	77	7	98	− 90	8	148	155	12	54	46
12	64	− 65	20	66	− 65	11	94	− 95	8	52	− 42	9	131	−133	13	83	72

Table 3. *(Continued)*

h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$	h k l	$\|F_o\|$	$\|F_c\|$
14 4 3	42	36	4 0 4	274	305	9 5 4	40	- 29	9 16 4	62	66	1 6 5	46	- 45	13 1 6	160	164
15	49	45	5	97	- 90	10	215	-227	2 17 4	61	- 63	2	44	42	14	66	58
16	49	47	7	35	- 27	11	110	102	5	70	- 78	1 7 5	72	67	15	45	- 41
19	67	- 54	8	121	-109	12	38	32	1 1 5	54	49	2	45	- 39	17	77	80
20	96	88	9	199	-202	13	88	- 81	3	59	57	3	57	49	19	51	43
21	50	38	10	60	- 24	15	155	157	4	42	45	4	46	49	21	95	97
23	91	- 90	11	208	-219	16	50	48	5	74	70	5	85	85	33	85	- 97
24	66	58	12	154	139	17	58	46	6	88	- 84	6	53	- 50	3 2 6	78	- 81
27	93	- 92	13	82	- 65	18	119	-116	8	58	55	8	68	69	4	60	- 58
2 5 3	69	- 59	16	180	-188	19	100	90	9	39	39	10	65	- 68	7	68	- 68
3	124	-115	17	64	- 23	22	74	66	11	50	- 48	11	50	- 50	8	29	31
4	44	- 32	19	67	- 59	23	93	89	12	68	62	12	64	64	11	68	- 70
5	59	- 52	21	133	136	24	57	53	14	68	- 65	15	67	- 71	16	40	37
6	56	- 43	22	75	65	25	75	64	15	81	- 82	18	51	- 53	17	50	- 49
9	72	72	24	161	-161	30	95	99	17	46	- 41	19	50	- 52	23	49	57
10	60	- 56	25	119	108	35	78	- 90	19	56	- 52	23	52	- 54	1 4 6	61	63
15	60	61	27	60	- 54	1 6 4	150	-158	1 2 5	88	88	1 8 5	85	88	3	86	- 92
17	82	74	29	107	122	2	60	- 58	2	117	-112	2	91	- 91	4	43	- 45
0 6 3	51	- 43	30	64	66	4	200	211	4	172	175	4	168	173	7	92	- 94
2	41	40	31	69	62	5	91	- 88	5	83	83	5	71	69	11	61	- 61
3	59	51	32	66	- 73	8	78	- 71	6	70	- 68	6	56	- 53	13	52	- 47
4	40	- 35	1 1 4	149	143	9	169	-176	7	52	46	7	53	53	19	48	47
11	47	39	2	85	78	11	148	-150	8	52	- 43	8	76	- 73	23	68	76
1 7 3	68	- 63	3	98	93	12	97	91	9	143	145	9	108	106	27	57	68
3	69	- 64	4	25	- 11	13	69	- 62	10	54	- 36	11	105	106	1 5 6	137	145
6	106	-106	5	159	161	16	137	-136	11	122	117	12	102	103	2	68	68
7	100	- 96	7	82	- 77	19	62	- 58	12	102	93	13	67	66	3	67	67
9	63	69	8	48	- 39	21	119	118	13	94	90	16	101	-102	5	60	- 57
10	90	- 85	9	65	52	22	58	50	14	43	27	21	72	- 77	6	81	- 78
11	59	- 57	10	186	190	24	132	-129	15	60	55	22	76	79	7	132	138
13	119	121	11	124	-106	25	92	85	16	102	- 95	24	116	-129	9	44	- 44
14	94	- 85	12	47	- 30	29	85	96	18	49	46	25	67	- 74	13	164	-170
17	89	90	13	36	25	1 7 4	100	101	21	95	- 97	29	65	- 73	14	103	-101
21	66	58	14	59	54	3	64	63	22	86	80	1 9 5	87	- 92	15	57	50
0 8 3	202	216	15	132	-133	5	62	58	24	110	-114	2	74	70	17	60	- 61
1	167	173	16	54	- 30	6	49	48	25	82	- 80	3	79	- 76	19	50	- 49
4	64	60	17	47	- 38	9	60	56	29	61	- 66	5	81	- 83	21	132	-138
5	68	- 54	18	77	77	10	76	71	1 3 5	116	-118	6	45	- 40	33	112	125
7	212	-222	19	103	-101	11	95	- 90	2	148	143	8	69	- 66	0 6 6	120	128
8	93	86	20	43	- 33	14	76	74	3	132	-129	10	134	134	1	139	-147
11	43	- 36	22	55	- 45	15	89	- 91	4	41	- 34	11	54	52	3	67	72
12	74	- 67	23	90	- 90	19	66	- 70	5	108	-103	12	61	- 59	5	51	52
13	131	-130	24	51	- 45	21	54	- 47	6	115	-110	15	75	77	7	161	166
14	49	- 34	25	49	- 37	5 8 4	60	55	7	37	24	16	56	- 58	8	69	68
15	100	- 97	30	65	- 67	7	43	47	8	108	-107	17	54	58	12	39	- 55
19	156	163	31	73	67	8	54	- 53	9	46	- 38	18	77	81	13	106	104
20	129	-128	35	80	89	9	52	54	10	229	248	19	66	77	15	79	81
21	76	- 78	0 2 4	100	- 99	11 9 4	50	- 51	11	95	84	23	76	74	19	106	-105
27	127	131	1	45	41	15	50	- 52	12	96	- 91	0 10 5	68	- 73	20	95	- 95
28	60	- 55	3	35	- 23	0 10 4	61	- 58	13	45	- 31	2	50	44	21	63	56
1 9 3	161	166	5	124	121	1	76	70	15	106	127	7	49	- 55	23	55	- 60
6	127	120	7	75	69	4	103	- 98	16	106	-100	9	69	- 66	27	126	-142
7	106	102	8	79	- 77	5	81	83	17	79	72	11	61	- 58	1 7 6	70	- 71
9	43	- 29	9	49	41	9	90	96	18	140	143	0 12 5	52	- 54	3	76	- 74
10	90	87	12	38	32	11	47	41	19	104	101	2 13 5	58	54	7	49	- 51
13	168	-177	13	48	47	15	48	49	21	70	66	3	58	- 53	9	58	58
14	119	115	15	71	62	16	54	58	22	87	- 80	10	80	- 89	10	46	49
15	66	61	20	75	74	21	70	- 78	23	94	82	4 14 5	108	113	13	80	83
19	69	- 71	25	63	- 64	24	69	73	25	50	40	9	77	83	17	63	74
21	105	-113	6 3 4	35	25	25	64	- 66	26	78	83	12	65	78	13 9 6	47	50
0 10 3	87	- 78	9	39	29	1 11 4	70	- 62	30	85	- 90	16	72	- 77	0 10 6	48	- 53
3	97	94	11	39	- 35	2	117	-110	35	68	- 71	1 0 6	181	-181	1	74	79
4	75	- 69	15	39	- 34	3	90	- 87	0 4 5	57	- 58	2	19	- 9	3	50	- 59
9	59	58	0 4 4	107	-104	5	116	-109	1	60	- 61	3	76	- 76	7	97	- 99
11	79	85	1	59	52	7	68	65	2	88	86	4	56	- 49	11	85	- 85
23	77	- 80	2	57	34	10	151	-165	4	79	- 74	5	74	66	13	60	- 61
0 12 3	54	- 45	3	36	- 26	11	61	59	5	71	- 74	7	215	226	19	62	70
3	69	66	4	78	- 71	13	61	- 63	6	51	48	8	87	82	27	71	85
1 13 3	60	- 64	5	134	132	15	103	113	7	47	- 45	11	45	45	1 11 6	111	109
6	74	- 74	6	42	31	17	53	47	9	115	-117	12	87	82	2	63	62
7	92	- 94	8	40	- 36	18	92	- 97	10	35	13	13	132	125	6	72	- 72
10	59	- 57	9	109	107	19	72	69	11	98	- 89	14	41	- 23	7	103	111
13	91	99	13	61	55	22	55	55	12	39	- 25	15	90	92	13	121	-133
14	86	- 86	15	83	79	23	69	77	13	83	- 82	16	68	61	14	76	- 86
21	75	87	16	46	38	1 12 4	70	- 68	15	57	- 55	19	134	-142	21	107	-125
0 14 3	120	113	19	44	43	4	87	86	16	44	52	20	112	-112	0 12 6	59	57
1	117	113	20	62	59	5	63	- 61	21	78	81	21	84	78	1	67	- 73
7	122	-124	21	73	- 72	9	91	- 94	22	61	- 52	23	58	- 58	7	85	84
8	66	62	24	54	46	11	78	- 76	24	58	56	27	138	-158	13	60	62
13	90	- 90	25	69	- 68	13	51	- 51	25	71	72	33	70	- 83	0 16 6	61	- 68
15	71	- 79	1 5 4	104	-103	16	54	- 54	2 5 5	45	45	1 1 6	138	-138	1	62	65
19	100	107	2	141	-140	21	68	71	3	40	41	2	28	- 21	7	80	- 89
20	92	- 97	3	137	-128	24	62	- 67	5	36	29	3	75	- 74			
1 15 3	63	57	5	150	-150	25	57	64	6	69	- 65	6	60	58			
1 0 4	240	-255	6	43	28	1 13 4	55	54	14	58	- 52	7	105	-106			
2	96	- 89	7	89	88	14	54	57	15	55	- 56	9	68	66			
3	58	25	8	50	45	4 16 4	82	- 88	0 6 5	58	- 60	11	33	- 33			

however, both positive and negative deviations are noted. It should be pointed out, though, that the excess bond strength (Type I oxygen atoms) is well compensated by the lengthening of the bonds involved. The excess bond strength or valence sum of 2.33, possessed by the

Table 4. *Interatomic distances and angles*

I. Ge(1) tetrahedron	
Ge—O(1)	1.732(17) Å
Ge—O(2)	1.695(15)
Ge—O(3)	1.802(14)
Ge—O(3′)	1.804(14)
Mean	1.758
O(2)—O(1)	2.93(2) Å
O(2)—O(3)	2.78(2)
O(2)—O(3′)	2.83(2)
O(1)—O(3)	2.90(2)
O(1)—O(3′)	2.82(2)
O(3)—O(3′)	2.96(2)
Mean	2.87
O(2)—Ge—O(1)	117.5(8)°
O(2)—Ge—O(3)	105.2(8)
O(2)—Ge—O(3′)	107.9(8)
O(1)—Ge—O(3)	110.2(8)
O(1)—Ge—O(3′)	105.5(8)
O(3)—Ge—O(3′)	110.5(8)
Mean	109.5

II. Ge(2) tetrahedron	
Ge—O(4)	1.745(12) Å
Ge—O(5)	1.687(14)
Ge—O(6)	1.780(12)
Ge—O(6′)	1.801(12)
Mean	1.753
O(5)—O(4)	2.94(2) Å
O(5)—O(6)	2.57(2)
O(5)—O(6′)	2.96(2)
O(4)—O(6)	2.95(2)
O(4)—O(6′)	2.89(2)
O(6)—O(6′)	2.80(2)
Mean	2.85
O(5)—Ge—O(4)	118.0(8)°
O(5)—Ge—O(6)	96.0(8)
O(5)—Ge—O(6′)	116.0(8)
O(4)—Ge—O(6)	113.8(8)
O(4)—Ge—O(6′)	109.2(8)
O(6)—Ge—O(6′)	102.7(8)
Mean	109.3

III. Mn(1) octahedron	
Mn—O(1)	2.298(17) Å
Mn—O(1′)	2.160(17)
Mn—O(2)	2.118(15)
Mn—O(4)	2.139(11)
Mn—O(4′)	2.188(11)
Mn—O(5)	2.146(14)
Mean	2.175
O(2)—O(4)	2.86(2) Å
O(2)—O(5′)	3.11(2)
O(2)—O(1′)	3.19(2)
O(2)—O(1)	3.31(2)
O(4)—O(5′)	3.23(2)
O(4)—O(4′)	3.16(2)
O(4)—O(1)	2.94(2)
O(5′)—O(1′)	2.96(2)
O(5′)—O(4′)	3.04(2)
O(1′)—O(4′)	2.94(2)
O(1′)—O(1)	3.22(2)
O(4′)—O(1)	2.90(2)
Mean	3.07(2)

IV. Mn(2) octahedron	
Mn—O(1)	2.182(17) Å
Mn—O(2)	2.104(15)
Mn—O(3)	2.429(14)
Mn—O(4)	2.228(11)
Mn—O(5)	2.160(14)
Mn—O(6)	2.329(13)
Mean	2.239
O(2)—O(1)	3.16(2) Å
O(2)—O(4)	2.86(2)
O(2)—O(6)	3.68(2)
O(2)—O(3)	3.55(2)
O(5)—O(1)	2.96(2)
O(5)—O(4)	2.99(2)
O(5)—O(6)	2.57(2)
O(5)—O(3)	3.22(2)
O(1)—O(4)	2.90(2)
O(1)—O(3)	3.24(2)
O(4)—O(6)	3.74(2)
O(6)—O(3)	2.91(2)
Mean	3.15(2)

Table 4. *(Continued)*

III. Mn(1) octahedron		IV. Mn(2) octahedron	
O(2)—Mn—O(4)	84.5(8)°	O(2)—Mn—O(1)	94.9(8)°
O(2)—Mn—O(5′)	93.6(8)	O(2)—Mn—O(4)	82.6(8)
O(2)—Mn—O(1′)	96.6(8)	O(2)—Mn—O(6)	112.2(8)
O(2)—Mn—O(1)	96.9(8)	O(2)—Mn—O(3)	102.8(8)
O(4)—Mn—O(5′)	97.6(8)	O(5)—Mn—O(1)	86.0(8)
O(4)—Mn—O(4′)	93.8(8)	O(5)—Mn—O(4)	85.8(8)
O(4)—Mn—O(1)	82.8(8)	O(5)—Mn—O(6)	69.6(8)
O(5′)—Mn—O(1′)	86.9(8)	O(5)—Mn—O(3)	89.0(8)
O(5′)—Mn—O(4′)	88.9(8)	O(1)—Mn—O(4)	82.3(8)
O(1′)—Mn—O(4′)	85.0(8)	O(1)—Mn—O(3)	89.1(8)
O(1′)—Mn—O(1)	92.6(8)	O(4)—Mn—O(6)	110.4(8)
O(4′)—Mn—O(1)	80.6(8)	O(6)—Mn—O(3)	75.3(8)
Mean	90.0	Mean	90.0
V. Ge—O—Ge angles		VI. O—O—O angles	
Ge(1)—O(3)—Ge(1)	123.4(7)	O(3)—O(3)—O(3)	135.0(9)
Ge(2)—O(6)—Ge(2)	129.7(7)	O(6)—O(6)—O(6)	156.8(9)

Table 5. *The valency sums of oxygen atoms*

Oxygen atoms	Balancing cations	Valencies charge coordination number	Total charges	Type
O(1)	Ge(1)	1	2.00	II
	2 Mn(1)	2/3		
	Mn(2)	1/3		
O(2)	Ge(1)	1	1.67	III
	2 Mn(1)	2/3		
O(3)	2 Ge(1)	2	2.33	I
	Mn(2)	1/3		
O(4)	Ge(2)	1	2.00	II
	2 Mn(1)	2/3		
	Mn(2)	1/3		
O(5)	Ge(2)	1	1.67	III
	Mn(1)	1/3		
	Mn(2)	1/3		
O(6)	2 Ge(2)	2	2.33	I
	Mn(2)	1/3		

tetrahedral linking (Type I) oxygen atom O(3) and O(6), is compensated by Mn(2)—O(3) and Mn(2)—O(6), the two longest bonds in the Mn(2) octahedra, and the two longest bonds in the Ge(1) and Ge(2) tetrahedra Ge(1)—O(3) and Ge(2)—O(6). Thus, if the lengthening of the bonds is taken into account, PAULING's rule is well satisfied.

Acknowledgments

The authors are obliged to A. TAUBER for supplying us single crystals of $MnGeO_3$ and to Dr. J. A. KOHN for his support and enthusiasm. We also thank Professor D. R. PEACOR for reviewing the manuscript.

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