krishna, 1969) for C–Br and between 1·73 Å (Schaefer, 1970) and 1·81 Å (Dejace, 1955) for C–Cl, taking only one example of the extreme cases. The present determinations seem to confirm the higher values.

The C–C–C bond angles with a mean value of 111·0 and 111·5° for DBD and DCD, respectively (Table 5), are in fairly good agreement with the mean value of 111·5° found for galactitol, verifying earlier observations of the widening of C–C–C bond angles in chain carbon molecules. The C–C–O bond angles, however, average 107·6 and 108·5° for DBD and DCD, respectively, being less than the tetrahedral angle as well as those reported for galactitol.

All oxygen atoms have two intermolecular oxygen neighbours in two directions nearly parallel to plane (001) and in hydrogen bond distances as it can be realized from Fig. 4 and Table 10. In this scheme of hydrogen bonding all oxygen atoms are involved as donors as well as acceptors resulting in closed circuits of hydrogen bondings. These closed circuits are all congruent and have their oxygen atoms at the corners of a parallelogram with an angle of 99·3° (Fig. 5, Table 10). From Figs. 4 and 5 it can be made clear that every molecule is always linked to four neighbouring molecules by two-two hydrogen bonds. In this way the closed circuits of hydrogen bondings result in two-dimensional networks of molecules. These networks are parallel to the (001) plane and are held together only by van der Waals forces.

The packing of the two-dimensional molecular networks is visualized in Fig. 4, from which it can also be realized that the neighbouring networks are contacted by the terminal halogen and hydrogen atoms of the chain molecules. The shortest intermolecular distances of these atoms are summarized for the two derivatives in Table 11. From these data it can be ascertained that between two neighbouring networks every molecule contacts three molecules of the neighbouring network. Two of these contacts are halogen–halogen and the third is halogen–hydrogen. The distances of these contacting atoms agree very well with the sum of the van der Waals radii in the case of DCD and are little shorter in DBD.

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Structure Determination of Mg_3TeO_6

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The structure of Mg_3TeO_6 has been determined by X-ray methods. Single crystals could be grown from NaCl or Na_2SO_4. Mg_3TeO_6 represents a new pseudocubic structure type; it is rhombohedral with $a_R = 6·05$ Å, $\alpha_R = 90°50'$, $Z=2$, $D_x = 4·46$ g.cm^{-3}, space group $R\bar{3}$. The final R value was equal to 4·8 %. Tellurium has a regular octahedral oxygen surrounding with Te–O = 1·91 Å. The coordination of Mg is a distorted octahedron with Mg–O distances varying between 2·02 and 2·28 Å. The thermal expansion characteristics were measured up to 820°C.

Introduction

Previous investigations on the crystal chemistry of tellurium oxides (Bayer, 1969) proved the existence of compounds $M^{2+}_3Te^{6+}O_6$ which can be derived from orthotelluric acid H_6TeO_6. Among these Ni_3TeO_6 has a corundum-type structure (Bayer, 1967; Newnham & Meagher, 1967; Kasper, 1968) and Cu_3TeO_6 crystallizes with the bixbyite structure (Bayer, 1967; Hostachy & Coing-Boyat, 1968), whereas Mg_3TeO_6 and Mn_3TeO_6 are isostructural and belong to a new structure type (Bayer, 1967; Kasper, 1968; Newnham, Dorrian & Meagher, 1970). Subsequent syntheses of isostructural compounds M_3SbO_6 were further evidence for the analogy of the crystal chemistry of Te^{6+} and Sb^{5+} (Kasper, 1968; Bayer, 1968).

A recent paper by Newnham, Dorrian & Meagher (1970) describes the crystal structure of Mg_3TeO_6 as determined from powder data. Powder data can only show the reflexion symmetry of the space group $R\bar{3}m$ but not of $R\bar{3}$. The similarity of the structure to rhombohedral Y_6UO_{12} was used as a guide line in that structure investigation. Single-crystal structure determination which was carried out at about the same time revealed some significant differences in atomic positions (Schulz & Bayer, 1970). In particular the Te–O distance was found to be quite normal (1·91 Å) as compared with the extremely short distance given by Newnham *et al.* (1970) (1·75 Å).

The details of the structure determination and the features of the Mg_3TeO_6 structure will be discussed in the following.

Experimental

Polycrystalline Mg_3TeO_6 can be prepared by heating a mixture $3MgO.1TeO_2$ in air at 650–800 °C. DTA/TGA runs proved that quantitative oxidation $Te^{4+} \rightarrow Te^{6+}$ occurs in the range 620–750 °C (heating rate $2°C.min^{-1}$). Mg_3TeO_6 starts to decompose by volatilization of TeO_2 above 950 °C. No transformation was found up to this temperature. Lattice constants were determined from Guinier powder photographs (Cu $K\alpha$ radiation silicon standard):

Mg_3TeO_6: $a_{\text{hex}} = 8{\cdot}615 \pm 0{\cdot}003$,
$c_{\text{hex}} = 10{\cdot}315 \pm 0{\cdot}003$ Å, $Z = 6$;
$a_R = 6{\cdot}05$ Å, $\alpha_R = 90°50'$, $Z = 2$;
$D_x = 4{\cdot}46$ g.cm^{-3}, $D_{\text{exp}} = 4{\cdot}33$ g.cm^{-3}.

For synthesis of single crystals polycrystalline Mg_3TeO_6 was mixed with an excess of NaCl or Na_2SO_4 and heated in a covered alumina crucible up to 950 °C for about 100 hours. After slowly cooling (about $5°C.hour^{-1}$) to room temperature platelet-like single crystals of hexagonal habit up to 1 mm in diameter could be leached out with hot water. The crystals grown from NaCl flux had more pronounced hexagonal habit and showed less twinning. Single crystals of about 0·2 mm in size were used for the crystal structure determination.

The reflexion intensities were measured with an off line single-crystal diffractometer (Siemens). The Nb-filtered radiation was generated by a Mo fine-focus tube at 50 kV. The diffractometer selects measuring time and weakening filter in order to measure the peak intensity of the reflexions with approximately the same count rate (40000 counts) and to get a dead-time loss of less than 1 %,

Table 1. *Observed and calculated structure factors*

H= 0 K= 0		
0	159	156
3	19	19
6	19	19
9	5	3
12	19	19
15	11	10
18	12	12
H= 0 K= 1		
2	80	79
5	5	4
8	0	0
11	5	3
14	6	8
17	3	6
20	2	3
H= 0 K= 2		
1	8	7
4	110	107
7	12	12
10	33	29
13	83	82
16	3	6
19	2	4
H= 0 K= 3		
0	3	6
3	2	3
6	30	29
9	33	29
12	11	12
15	17	15
18	19	19
H= 0 K= 4		
2	76	76
5	76	76
8	0	0
11	4	2
14	4	2
17	80	79
H= 0 K= 5		
1	159	156
4	100	95
7	2	4
10	55	53
13	8	4
16	110	107
19	80	78
H= 0 K= 6		
0	2	4
3	11	12
6	8	7
9	6	7
12	6	7
15	159	156
18	12	13
H= 0 K= 7		
2	11	12
5	17	15
8	110	107
11	3	6
14	100	96
17	76	76
H= 0 K= 8		
1	7	4
4	7	7
7	0	0
10	4	2
13	100	95
16	6	7
H= 0 K= 9		
0	5	3
3	101	97
6	151	151
9	8	4
12	53	51
15	2	4
H= 0 K= 10		
2	5	8
5	5	8
8	6	7
11	5	4
14	8	8
H= 0 K= 11		
1	28	26
4	32	30
7	110	107
10	11	12
13	17	15
H= 0 K= 12		
0	18	18
3	8	7
6	7	4
9	7	7
12	5	5
H= 0 K= 13		
2	13	15
5	100	95
8	9	8
H= 0 K= 14		
1	5	3
4	151	151
H= 1 K= 0		
4	17	17
7	53	51
10	5	3
13	8	7
16	5	6
19	5	8
H= 1 K= 1		
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-15	5	8
-12	19	19
-9	24	23
-6	32	30
-3	9	6
0	2	3
3	18	18
6	148	146
9	105	101
12	7	5
15	18	18
18	10	12
H= 1 K= 2		
-19	9	6
-16	9	6
-13	18	3
-10	6	1
-7	74	71
-4	53	51
-1	0	0
2	19	18
5	5	6
8	60	59
11	9	8
14	5	6
17	19	19
20	5	5
H= 1 K= 3		
-17	24	23
-14	4	2
-11	10	9
-8	3	6
-5	0	0
-2	0	0
1	60	59
4	8	0
7	18	18
10	7	5
13	9	6
16	9	6
19	8	7
H= 1 K= 4		
-18	29	28
-15	5	3
-12	93	91
-9	16	15
-6	0	0
-3	60	59
0	13	15
3	17	18
6	0	0
9	105	101
12	2	3
15	5	6
18	10	3
H= 1 K= 5		
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-16	111	110
-13	29	28
-10	60	59
-7	0	0
-4	12	12
-1	60	59
2	5	3
5	9	6
8	60	59
11	6	1
14	149	145
17	93	91
H= 1 K= 6		
-17	87	85
-14	16	15
-11	3	2
-8	13	15
-2	14	13
1	8	4
4	53	52
7	17	18
10	5	6
13	13	15
16	14	15
H= 1 K= 7		
-15	111	110
-12	20	17
-9	111	110
-6	95	93
-3	46	45
0	0	0
3	30	28
6	12	12
9	60	59
12	74	71
15	6	8
H= 1 K= 8		
-16	5	3
-13	74	71
-10	9	6
-7	6	4
-4	12	13
-1	101	97
2	12	12
5	53	51
8	111	110
11	6	4
14	13	15
H= 1 K= 9		
-14	76	76
-11	9	10
-8	9	10
-5	9	6
-2	27	24
1	46	45
4	0	0
7	46	45
10	95	93
13	10	7
H= 1 K= 10		
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-6	5	3
-3	77	71
0	11	11
3	27	24
6	12	10
9	101	97
12	14	16
H= 1 K= 11		
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-4	111	110
-1	6	4
2	87	85
5	148	146
8	10	9
11	9	10
H= 1 K= 12		
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-8	87	85
-5	5	7
-2	22	22
1	46	45
4	115	108
7	9	6
10	12	12
H= 1 K= 13		
-6	0	0
-3	46	45
0	91	88
3	18	13
6	6	6
H= 1 K= 14		
-4	89	93
-1	27	24
2	16	15
H= 2 K= 0		
2	12	12
5	35	37
8	111	110
11	36	33
14	77	71
17	148	146
20	11	5
H= 2 K= 1		
-20	35	37
-17	91	86
-14	74	71
-11	60	59
-8	148	146
-2	79	81
1	9	8
4	11	9
7	22	22
10	46	45
13	91	88
16	74	71
19	9	8
H= 2 K= 2		
-18	89	93
-15	80	78
-12	7	8
-9	9	6
-6	68	70
-3	14	13
0	13	15
3	16	17
6	18	13
9	13	12
12	13	15
15	35	37
18	87	85
H= 2 K= 3		
-19	17	18
-16	4	2
-13	79	81
-10	115	108
-7	11	9
-4	4	2
-1	9	8
2	16	17
5	74	71
8	91	88
11	84	86
14	143	141
17	80	78
H= 2 K= 4		
-17	22	22
-14	89	93
-11	54	50
-8	54	50
-5	14	13
-2	7	8
1	9	8
4	5	3
7	13	15
10	77	71
13	87	85
16	17	18
19	9	8
H= 2 K= 5		
-18	83	81
-15	14	16
-12	16	9
-9	4	2
-6	5	3
-3	10	12
0	83	81
3	74	71
6	17	18
9	80	79
12	87	85
15	22	22
18	115	108
H= 2 K= 6		
-16	54	50
-13	16	15
-10	14	13
-7	18	18
-4	54	50
-1	5	3
2	46	45
5	13	15
8	87	85
11	9	8
14	100	95
17	5	4
H= 2 K= 7		
-17	16	9
-14	46	45
-11	16	18
-8	25	25
-5	83	81
-2	74	71
1	17	18
4	95	97
7	87	85
10	18	18
13	95	97
16	84	80
H= 2 K= 8		
-15	16	15
-12	11	7
-9	80	78
-6	54	50
-3	8	7
0	5	4
3	35	37
6	9	6
9	46	45
12	26	18
15	18	19
H= 2 K= 9		
-13	16	9
-10	7	5
-7	16	18
-4	25	25
2	16	9
5	16	18
8	61	56
11	4	2
14	87	85
H= 2 K= 10		
-11	13	13
-8	95	97
-5	15	15
-2	25	24
1	11	7
4	8	1
7	80	78
10	25	25
13	5	4
H= 2 K= 11		
-9	13	15
-6	35	37
-3	35	37
0	26	18
3	13	14
6	14	16
9	34	32
H= 2 K= 12		
-7	89	93
-4	9	10
2	25	25
5	25	25
8	16	18
H= 2 K= 13		
-5	9	6
-2	148	146
4	69	69
H= 3 K= 0		
3	14	16
6	5	5
9	25	24
12	111	91
15	20	20
18	148	146
H= 3 K= 1		
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-16	7	5
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-1	13	14
2	86	78
5	12	12
8	14	16
11	31	29
14	30	30
17	5	5
H= 3 K= 2		
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-14	93	89
-11	18	18
-8	8	7
-5	148	146
-2	90	89
1	83	76
4	111	91
7	5	3
10	14	16
13	58	57
16	58	57
19	7	5
H= 3 K= 3		
-18	25	24
-15	9	6
-12	5	7
-9	19	19
-6	5	3
-3	12	12
0	14	16
3	148	146
6	18	16
9	30	30
12	27	24
15	115	113
18	18	18
H= 3 K= 4		
-16	8	7
-13	20	17
-10	93	89
-7	83	74
-4	5	8
-1	9	6
2	54	53
5	54	53
8	58	57
11	7	10
14	54	53
17	25	24
H= 3 K= 5		
-17	20	20
-14	19	19
-11	93	96
-8	13	13
-5	61	56
-2	14	16
1	18	16
4	56	55
7	25	25
10	12	12
13	82	84
16	49	46
H= 3 K= 6		
-15	8	7
-12	68	68
-9	8	7
-6	5	8
-3	94	95
0	83	76
3	23	22
6	5	8
9	5	3
12	79	81
15	54	50
H= 3 K= 7		
-16	4	2
-13	54	50
-10	20	19
-7	9	6
-4	4	2
-1	9	10
2	88	89
5	56	55
8	13	13
11	6	5
14	13	14
H= 3 K= 8		
-14	53	52
-11	4	5
-8	68	69
-5	8	7
-2	29	27
1	4	5
4	153	147
7	5	3
10	68	70
13	24	25
H= 3 K= 9		
-12	79	81
-9	80	78
-6	4	2
-3	5	7
0	91	91
3	4	2
6	4	2
9	82	84
12	54	53
H= 3 K= 10		
-10	66	66
-7	20	17
-4	56	55
-1	23	23
2	53	52
5	20	17
8	34	32
11	18	18
H= 3 K= 11		
-8	29	27
-5	63	62
-2	153	147
1	5	3
4	94	95
7	153	147
10	83	76
H= 3 K= 12		
-6	65	65
-3	54	53
0	88	89
3	8	7
6	57	52
H= 3 K= 13		
-1	4	2
2	80	78
H= 4 K= 0		
1	57	56
4	32	30
7	70	66
10	56	56
13	14	14
16	61	56
19	9	10
H= 4 K= 1		
-18	34	32
-15	20	17
-12	71	69
-9	65	61
-6	23	20
-3	66	66
0	34	32
3	63	62
6	45	43
9	3	3
12	45	43
15	35	37
18	54	53
H= 4 K= 2		
-19	8	7
-16	76	75
-13	2	1
-10	14	14
-7	32	30
-4	66	67
-1	63	62
2	57	56
5	61	56
8	26	26
11	70	66
14	13	15
17	71	69
H= 4 K= 3		
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-14	66	66
-11	10	12
-8	34	32
-5	20	17
-2	29	27
1	69	64
4	45	43
7	35	37
10	3	3
13	34	32
16	153	147
H= 4 K= 4		
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-15	19	19
-12	57	56
-9	20	20
-6	73	69
-3	8	7
0	61	56
3	26	26
6	10	9
9	57	56
12	32	32
15	14	14
18	16	14
H= 4 K= 5		
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-13	99	98
-10	25	25
-7	66	67
-4	25	23
-1	89	93
2	66	67
5	32	32
8	16	14
11	66	66
14	53	51
17	29	27
H= 4 K= 6		
-14	80	79
-11	87	90
-8	76	75
-5	20	20
-2	8	7
1	25	25
4	17	15
7	61	56
10	89	86
13	16	9
16	57	56
H= 4 K= 7		
-15	25	23
-12	66	66
-9	15	13
-6	53	50
-3	25	23
0	25	23
3	66	67
6	32	32
9	16	14
12	93	91
15	53	51
H= 4 K= 8		
-13	20	20
-10	16	14
-7	57	55
-4	87	90
-1	20	17
2	88	88
5	102	101
8	17	15
11	8	7
14	74	75
H= 4 K= 9		
-11	25	25
-8	25	25
-5	56	55
-2	66	66
1	69	69
4	15	13
7	31	31
10	25	23
H= 4 K= 10		
-9	90	89
-6	66	67
-3	76	75
0	16	9
3	78	75
6	24	23
H= 4 K= 10		
9	10	9
H= 4 K= 11		
-7	80	79
-4	78	75
-1	77	74
2	20	17
5	102	101
8	57	56
H= 4 K= 12		
-5	6	2
-2	63	64
1	18	19
4	25	25
H= 5 K= 0		
2	91	92
5	19	19
8	69	69
11	93	91
14	31	31
17	56	55
H= 5 K= 1		
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-14	33	31
-11	18	17
-8	16	9
-5	11	10
-2	24	23
1	43	43
4	18	17
7	74	76
10	80	79
13	20	17
16	66	67
19	63	64
H= 5 K= 2		
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-15	78	75
-12	78	75
-9	15	13
-3	9	6
0	54	50
3	89	93
6	80	79
9	91	92
12	66	66
15	9	6
18	6	2
H= 5 K= 3		
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-13	17	15
-10	17	15
-7	6	2
-4	80	79
-1	18	17
2	11	10
5	17	15
8	43	43
11	24	23
14	78	75
17	16	9
H= 5 K= 4		
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-14	78	75
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-8	16	14
-5	54	58
-2	62	61
1	80	79
4	16	9
7	25	23
10	78	75
13	93	91
16	66	67
H= 5 K= 5		
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-12	25	23
-9	17	15
-6	18	17
-3	19	19
0	11	10
3	18	17
6	47	46
9	17	15
12	34	32
15	65	65
H= 5 K= 6		
-13	90	89
-10	6	2
-7	81	79
-4	90	89
-1	54	53
2	16	14
5	90	89
8	56	54
11	83	80
14	54	50
H= 5 K= 7		
-14	93	91
-11	18	18
-8	16	9
-5	25	23
-2	9	9
1	73	69
4	108	109
7	41	44
10	19	19
13	47	46
H= 5 K= 8		
-12	18	17
-9	17	15
-6	18	19
-3	83	82
0	11	11
3	74	71
6	11	11
9	90	89
12	16	14
H= 5 K= 9		
-10	54	53
-7	90	89
-4	83	82
-1	13	14
2	0	0
5	60	59
8	55	53
11	80	79
H= 5 K= 10		
-8	9	0
-5	74	76
-2	108	109
4	62	59
7	93	91
H= 5 K= 11		
-6	91	85
-3	18	17
0	17	14
3	93	91
6	56	54
H= 6 K= 0		
3	11	11
6	83	82
9	11	11
12	42	43
15	17	15
18	83	80
H= 6 K= 1		
-16	74	76
-13	83	82
-10	20	21
-7	5	6
-4	17	13
-1	74	69
2	60	59
5	12	12
8	13	14
11	74	71
14	31	32
17	56	55
H= 6 K= 2		
-17	63	64
-14	11	10
-8	41	39
-5	70	71
-2	78	80
1	93	91
4	67	69
7	70	71
10	42	43
13	17	15
16	13	11
H= 6 K= 3		
-15	5	4
-12	9	8
-9	74	69
-6	20	21
-3	13	14
0	13	14
3	74	69
6	20	21
9	5	6
12	74	76
15	31	32
H= 6 K= 4		
-16	69	66
-13	63	64
-10	96	95
-7	41	39
-4	82	80
-1	78	80
2	8	7
5	67	69
8	70	71
11	13	12
14	9	8
H= 6 K= 5		
-14	93	91
-11	13	15
-8	0	0
-5	9	8
-2	64	64
1	25	22
4	63	63
7	13	14
10	20	21
13	108	109
H= 6 K= 6		
-12	70	66
-9	96	95
-6	63	64
-3	63	64
0	63	64
3	41	39
6	9	11
9	70	64
12	8	7
H= 6 K= 7		
-13	63	64
-10	67	69
-7	65	65
-4	20	21
-1	70	66
2	13	16
5	0	0
8	0	0
11	6	4
H= 6 K= 8		
-11	67	69
-8	63	63
-2	22	22
1	25	22
4	25	25
7	78	75
10	72	69
H= 6 K= 9		
-9	12	12
-6	63	64
-3	72	69
0	82	80
3	9	11
6	78	64
9	11	11
H= 6 K= 10		
-4	9	11
-1	83	82
2	63	64
5	20	21
H= 7 K= 0		
1	74	73
4	13	16
7	10	9
10	0	0
13	9	8
16	55	53
H= 7 K= 1		
-15	70	64
-12	22	22
-9	81	78
-6	25	25
-3	83	82
0	108	104
3	70	64
6	14	15
12	72	69
15	11	10
H= 7 K= 2		
-16	8	7
-13	5	4
-10	69	66
-7	9	11
-4	66	67
-1	76	75
2	83	82
5	5	4
8	27	27
11	10	9
14	83	82
17	134	134
H= 7 K= 3		
-14	55	53
-11	14	15
-8	13	16
-5	81	78
-2	12	12
1	83	82
4	14	15
7	108	104
10	90	93
16	68	59
H= 7 K= 4		
-15	83	82
-12	80	80
-9	5	4
-6	5	4
-3	70	70
0	69	66
3	66	67
6	49	53
9	5	4
12	87	90
15	76	73
H= 7 K= 5		
-13	83	82
-10	53	52
-7	80	78
-4	72	69
-1	16	18
2	80	78
5	13	13
8	13	13
11	81	76
14	108	104
H= 7 K= 6		
-8	9	11
-5	16	18
-2	16	18
1	74	71
4	85	83
7	95	95
10	80	80
13	69	66
H= 7 K= 7		
-9	12	12
-6	66	67
-3	5	4
0	69	66
3	14	14
6	80	79
H= 7 K= 8		
-7	53	52
-4	9	7
-1	86	86
2	81	79
5	80	78
8	11	11
H= 7 K= 9		
-5	13	13
-2	83	82
1	15	18
4	7	5
7	69	66
H= 7 K= 10		
0	16	18
H= 8 K= 0		
2	8	0
5	85	83
8	69	68
11	95	95
14	89	92
17	9	11
H= 8 K= 1		
-14	74	71
-11	7	5
-8	5	0
-5	66	67
-2	5	0
1	93	91
4	9	7
7	86	86
10	69	66
13	68	70
16	11	11
H= 8 K= 2		
-15	75	76
-12	82	84
-9	71	68
-6	7	5
-3	80	78
0	71	68
3	65	61
6	0	0
9	69	68
12	68	70
15	95	95
H= 8 K= 3		
-13	134	134
-10	75	76
-7	64	64
-4	85	88
-1	75	76
2	7	5
5	83	80
8	5	0
11	8	7
14	12	11
H= 8 K= 4		
-14	68	70
-11	8	4
-8	68	70
-5	16	18
-2	19	19
1	93	96
4	69	66
7	71	68
10	65	65
13	93	91
H= 8 K= 5		
-12	7	4
-9	68	70
-6	65	61
-3	81	80
0	134	134
3	7	4
6	9	10
9	85	88
12	13	12
H= 8 K= 6		
-10	83	81
-7	9	11
-4	22	23
-1	53	52
2	75	76
5	78	71
8	76	74
11	68	70
H= 8 K= 7		
-8	99	103
-5	19	19
-2	82	84
1	19	19
4	93	96
7	57	52
H= 8 K= 8		
-6	69	66
-3	13	11
0	95	95
3	68	70
6	80	79
H= 8 K= 9		
-1	6	9
2	83	80
H= 9 K= 0		
3	108	106
6	7	4
9	83	81
12	9	11
15	89	86
H= 9 K= 1		
-13	53	52
-10	7	5
-7	13	12
-4	76	74
-1	76	74
2	99	103
5	15	16
8	10	8
11	8	0
14	81	78
H= 9 K= 2		
-14	69	66
-11	53	51
-8	66	67
-5	95	95
-2	99	98
1	85	88
4	53	51
7	68	70
10	6	9
13	71	68
H= 9 K= 3		
-12	78	71
-9	8	11
-6	83	81
-3	112	109
0	7	5
3	79	77
6	76	74
9	80	79
12	76	74
H= 9 K= 4		
-10	15	14
-7	10	8
-4	84	83
-1	30	30
2	66	62
5	15	14
8	53	51
11	13	11
H= 9 K= 5		
-11	79	77
-8	16	14
-5	14	16
-2	53	51
1	99	98
4	5	4
7	109	109
10	78	71
H= 9 K= 6		
-9	19	22
-6	57	52
-3	65	65
0	79	77
3	112	109
6	69	67
9	9	10
H= 9 K= 7		
-7	79	77
-4	81	78
-1	84	83
2	76	74
5	6	9
H= 9 K= 8		
-2	19	22
1	15	14
H= 10 K= 0		
1	70	64
4	70	69
H= 10 K= 0		
7	88	93
10	69	66
13	80	78
H= 10 K= 1		
-12	5	4
-9	5	4
-6	99	98
-3	78	78
0	78	78
3	66	67
6	5	4
9	5	8
12	65	65
H= 10 K= 2		
-13	75	76
-10	0	0
-7	69	64
-4	91	91
-1	66	67
2	84	83
5	69	64
8	103	104
11	97	94
H= 10 K= 3		
-11	13	16
-8	78	64
-5	88	93
-2	0	0
1	16	14
4	17	17
7	5	6
10	112	109
H= 10 K= 4		
-9	0	0
-6	78	78
-3	0	0
0	5	6
3	5	4
6	0	0
9	6	2
H= 10 K= 5		
-7	0	0
-4	76	74
-1	0	0
2	75	76
5	0	0
8	57	52
H= 10 K= 6		
-5	65	65
-2	0	0
1	65	65
4	97	94
H= 10 K= 7		
0	73	68
H= 11 K= 0		
2	0	0
5	27	29
8	10	10
H= 11 K= 1		
-8	5	0
-5	19	22
-2	53	52
1	53	52
4	103	104
7	5	0
10	0	0
H= 11 K= 2		
-9	53	52
-6	0	0
-3	8	0
0	76	74
3	13	14
6	109	109
9	0	0
H= 11 K= 3		
-10	0	0
-7	69	64
-4	75	76
-1	0	0
2	103	103
5	65	65
8	95	95
H= 11 K= 4		
-8	9	6
-5	0	0
-2	0	0
1	27	29
4	53	52
7	9	11
H= 11 K= 5		
-6	53	52
-3	0	0
0	86	83
3	5	0
6	65	61
H= 12 K= 0		
-3	0	0
6	103	104
9	0	0
12	75	76
H= 12 K= 1		
-10	70	70
-7	0	0
-4	0	0
-1	70	70
2	102	101
8	86	81
11	9	6
H= 12 K= 2		
-8	13	14
-2	9	6
1	66	66
4	79	77
7	0	0
H= 12 K= 3		
-6	46	45
-3	46	45
0	86	81
3	0	0
6	0	0
H= 12 K= 4		
-4	53	52
-1	0	0
2	89	86
H= 13 K= 0		
1	0	0
4	0	0
7	0	0
H= 13 K= 1		
-6	0	0
-3	0	0
0	0	0
3	0	0
6	0	0
H= 13 K= 2		
-4	70	70
2	0	0
5	0	0
H= 13 K= 3		
-2	0	0
1	10	8
H= 14 K= 0		
2	0	0
5	13	14
H= 14 K= 1		
-2	0	0
1	9	6
4	86	81

The crystal investigated was shaped like a sphere with a radius of about 150μ. All reflexions with $l \geq 0$ up to $\theta = 40°$ were measured.

The absorption correction for a crystal sphere was applied to the 1195 observed, unweighted, non-symmetry equivalent intensity mean values derived from about 4000 single measurements. An intensity mean value was considered as 'observed', if its intensity was larger than its threefold standard deviation. Their weights were usually calculated from the impulse rates. In cases where twice the estimated standard deviation of the symmetry equivalent reflexions was larger than the standard deviation of the counting statistics the e.s.d. was used as weight.

Thermal expansion measurements were carried out on a heating diffractometer with Cu $K\alpha$-radiation (Philips unit, MCR high temperature X-ray furnace). The temperature was calibrated for the range 20–900°C; polycrystalline α-Al_2O_3 was used as a standard. The 2θ range 19 to 50° was scanned at 200°C intervals from 20°C to 820°C and back. The positions of 10 reflexions in this range were measured and used for calculation of lattice constants at the various temperatures. Satisfactory and reproducible results (maximum deviation in lattice constants ±3%) were obtained when two or three adjacent reflexions were used for calculation of lattice constants and plotted *versus* temperature, *e.g.* 110, 012; 122, 104; 312, 214. The results of the measurements are shown in Fig. 1. The average linear thermal expansion coefficients between 20 and 820°C are

$$\beta_a = 7{\cdot}3 \pm 0{\cdot}2 \times 10^{-6}\,°C^{-1}$$
$$\beta_c = 10{\cdot}5 \pm 0{\cdot}3 \times 10^{-6}\,°C^{-1}\,.$$

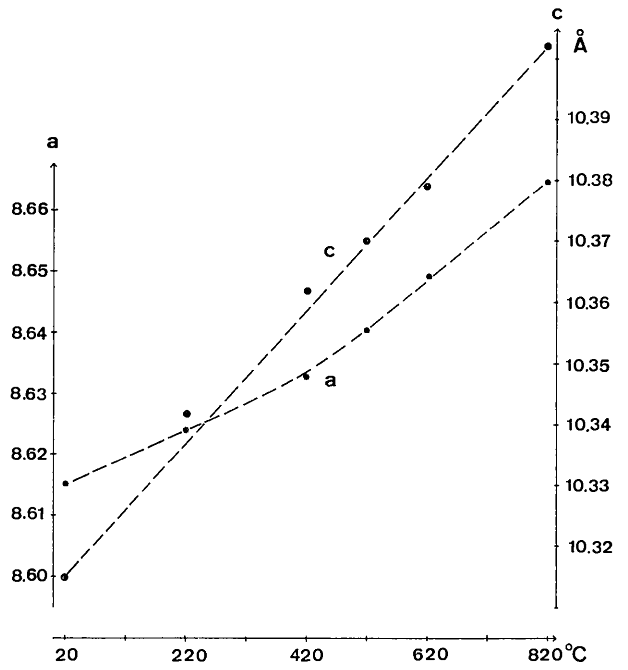


Fig. 1. Temperature dependence of the lattice constants.

Table 2. *Structure parameters*

The numbers in brackets are the standard deviations in units of the last digit. The coefficients of the anisotropic temperature factors are calculated with the equation $T = \exp\,[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

	Atomic position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te(1)	3(*a*)	0·0	0·0	0·0	0·00120 (6)	$=\beta_{11}$	0·00095 (5)	$=\beta_{11}$	0·0	0·0
Te(2)	3(*b*)	0·0	0·0	0·5	0·0013 (6)	$=\beta_{11}$	0·00086 (5)	$=\beta_{11}$	0·0	0·0
O(1)	18(*f*)	0·2008 (5)	0·1712 (5)	0·0989 (3)	0·0016 (4)	0·0027 (4)	0·0015 (2)	0·0011 (7)	−0·0005 (5)	−0·0008 (5)
O(2)	18(*f*)	0·1853 (5)	0·1599 (4)	0·6155 (3)	0·0022 (4)	0·0024 (4)	0·0014 (2)	0·0022 (7)	−0·0001 (5)	−0·0003 (5)
Mg	18(*f*)	0·4015 (2)	0·1081 (2)	0·0449 (2)	0·0025 (2)	0·0024 (2)	0·0016 (1)	0·0028 (4)	0·0001 (3)	0·0001 (3)

Extinction parameter $g = 8{\cdot}6\ (3) \times 10^{-6}$

Table 3. *Magnitudes and direc*

The numbers in brackets are the standard deviations in units of the last digit.

	Te(1)			Te(2)		
Length of the main axes (Å)	0·0582 (2)	0·0582 (2)	0·0734 (2)	0·0695 (1)	0·0605 (1)	0·0697 (2)
Angle with						
axis 1 (°)	90	90	0	90	90	0
axis 2 (°)	—	—	90	—	—	90
axis 3 (°)	—	—	90	—	—	90

The anisotropy of thermal expansion (1/1·44) is quite pronounced and points to a stronger bond within the layers parallel to (0001) as compared with the *c* axis which runs perpendicular to these layers.

Mg_3TeO_6 has a reasonably close packed structure with a packing density of 62%. This in comparison to the less dense structure of MgO which has $P=52\%$ and a rather high thermal expansion of about $13 \times 10^{-6}\,°C^{-1}$. Probably the small, high valent tellurium cations exert an inhibiting effect on the thermal motion of Mg^{2+} and O^{2-} especially in the **a** direction.

Structure determination

The diffraction pattern points to the space groups $R3$ or $R\bar{3}$. The true space group was determined by the centre test of Karle, Dragonette & Brenner (1965). For this and all further calculations the ionic states Te^{6+}, Mg^{2+}, O^{2-} were assumed. The scattering curves for Te^{6+} and Mg^{2+} were taken from Thomas & Umeda (1957), and those for O^{2-} from Tokonami (1965). The following results were obtained: average $|E|^2=1{\cdot}013$, average $|E^2-1|=0{\cdot}945$, average $|E|=0{\cdot}808$, which means that the structure is centrosymmetric.

The hexagonal elementary cell contains 6 Te atoms. In the space group $R\bar{3}$ they can occupy the sixfold atomic position 6(*c*) or the two threefold atomic positions 3(*a*) and 3(*b*). A Patterson synthesis should show in the first case two strong Te–Te maxima in $(0,0,\pm 2z)$ (and the corresponding symmetry equivalent maxima) and in the second case one Te–Te maximum in $(0,0,\frac{1}{2})$. The Patterson synthesis shows a maximum in $(0,0,\frac{1}{2})$ and therefore the Te atoms were put into the atomic positions 3*a* and 3*b*. There are always two Te atoms with the coordinates (x,y,z) and $(x,y,z+\frac{1}{2})$, for the Te atoms therefore the **c** direction is divided into equal halves. They do not contribute to the intensity of the reflexions with $l=2n+1$.

A structure factor calculation using only reflexions with $l=2n$ and the Te atoms lead to an unweighted *R* value of 0·19. The corresponding Fourier synthesis showed 6 maxima around each Te atom, altogether 18 maxima, occupying one general position 18(*f*). The distance to the Te atoms equals 1·9 Å, which corresponds to the normal Te–O distances (Table 5). A Fourier synthesis with $l=2n$ reflexions is equal to a 'projection' of the structure into a subcell with the coordinates $(a,b,c/2)$. Therefore the subcell should contain 36 O maxima around the Te atoms, but only 18 could be found. From this follows that also the O atoms halve (approximately or exactly) the **c** direction. The Fourier synthesis revealed 18 other maxima in the general position 18(*f*). They were interpreted as Mg positions. A least-squares refinement using $l=2n$ reflexions and the Te and O atoms with an atomic position multiplier equal to 2·0 and the Mg atoms with a multiplier equal to 1·0 resulted in $R=0{\cdot}08$. The scale factor, the atomic positions and the individual temperature factors were refined.

The Mg atoms were used to determine the signs of the reflexions with $l=2n+1$. A corresponding structure factor calculation resulted in $R=0{\cdot}32$. The Fourier synthesis contained Mg maxima and besides the O positions (determined from the $l=2n$ reflexions) weak maxima showing the O atoms do not exactly halve the **c** direction. The O atoms were shifted in the direction of these maxima. In this manner they fall into two general positions 18(*f*) with different (x,y,z) coordinates. A least-squares refinement with the Te and Mg atoms and the O atoms in their new position using only $l=2n+1$ reflexions and all reflexions lead to *R* values of 0·11 and 0·07 respectively. The normal least-squares refinement procedure was then started with individual weights including the secondary extinction parameter *g* (Zachariasen, 1963; Larson, 1967). The Te atoms were corrected for anomalous dispersion with the values given by Cromer (1965). The equations used for the refinement are described in Roof, Larson & Cromer (1968). The results are listed in Tables 1 to 4. The final agreement factors were equal to unweighted $R=0{\cdot}048$, weighted $R=0{\cdot}041$, Hamilton's $R=0{\cdot}052$, (Hamilton, 1965).

Table 4. *Interatomic distances and angles*

The numbers in brackets are the standard deviations in units of the last digit.

Te(1) Octahedron	
Te(1)—O(1^{i})	1·912 (3) Å
O(1^{i})—O(1^{ii})	2·603 (5)
O(1^{i})—O(1^{iii})	2·801 (5)
O(1^{ii}) -Te(1)-O(1^{iii})	85·8 (1)°
O(1^{ii}) -Te(1)-O(1^{iv})	94·2 (1)
Te(2) Octahedron	
Te(2)—O(2^{i})	1·914 (3) Å
O(2^{i})—O(2^{ii})	2·813 (5)
O(2^{i})—O(2^{iii})	2·596 (4)
O(2^{ii}) -Te(2)-O(2^{iii})	94·6 (1)°
O(2^{ii}) -Te(2)-O(2^{iv})	85·4 (1)
Mg Octahedron	

tions of the thermal main axes

Orthogonal reference system: axis 1 c axis; axis 2 a_1 axis; axis 3 a_2^* axis.

O(1)			O(2)			Mg		
0·064 (9)	0·088 (12)	0·103 (13)	0·078 (8)	0·081 (19)	0·090 (9)	0·077 (11)	0·084 (4)	0·094 (3)
75 (16)	148 (30)	117 (33)	69 (54)	115 (56)	33 (42)	91 (25)	73 (21)	17 (20)
45 (15)	61 (22)	121 (25)	50 (>90)	41 (>90)	84 (64)	143 (25)	126 (28)	81 (22)
49 (13)	101 (30)	44 (12)	47 (>90)	120 (>90)	122 (32)	53 (25)	139 (26)	76 (20)

Table 4 (*cont.*)

Mg —O(1^{v})	2·022 (4) Å
Mg —O(2^{viii})	2·049 (3)
Mg —O(2^{vi})	2·124 (4)
Mg —O(1^{ii})	2·130 (5)
Mg —O(2^{vii})	2·159 (4)
Mg —O(1^{i})	2·278 (4)
O(2^{vii})-O(2^{vi})	2·596 (4) Å
O(1^{i})—O(1^{ii})	2·604 (5)
O(2^{vii})-O(2^{viii})	2·710 (7)
O(1^{v})—O(1^{ii})	2·712 (9)
O(1^{i})—O(2^{viii})	2·775 (5)
O(1^{ii}) -O(2^{vi})	2·775 (6)
O(1^{v})—O(2^{viii})	3·016 (5) Å
O(1^{i})—O(2^{vi})	3·182 (6)
O(1^{v})—O(2^{vi})	3·329 (5)
O(1^{v})—O(2^{vii})	3·342 (5)
O(1^{i})—O(2^{vii})	3·576 (5)
O(1^{ii}) -O(2^{viii})	3·661 (6)
O(1^{i})—Mg —O(1^{v})	144·8 (2)°
O(2^{vii})-Mg —O(2^{vi})	74·6 (1)
O(2^{vii})-Mg —O(2^{viii})	80·2 (2)
O(1^{ii}) -Mg —O(2^{vi})	81·4 (1)
O(1^{ii}) -Mg —O(2^{viii})	122·3 (2)

The structure determination was carried out with the following computer programs: (1) Symbolic Addition Procedure of the NRC of Canada by S. R. Hall; (2) Fourier program made available by R. Jacobson, Department of Chemistry, Iowa State University; (3) Los Alamos Crystal Structure least-squares program *GENLES* by A. C. Larson; (4) Function and Error Program by Busing & Levy.

Discussion

The structure of Mg_3TeO_6 is built up from TeO_6 and MgO_6 octahedra. With respect to the oxygen arrangement, the structure definitely contains elements of hexagonal close packing with strongly distorted oxygen layers parallel to (0001). This explains the reasonably high packing density of 62%.

The Te^{6+} ions show a very regular, octahedral oxygen surrounding [Fig. 2(*b*)] with Te–O = 1·91 Å (Table 4). This is in good agreement with Te–O distances observed in other Te-containing oxide compounds, but deviates strongly from the 1·75 Å given for Mg_3TeO_6 by Newnham *et al.* (1970). Table 5 lists the Te–O distances reported so far in the literature.

The MgO_6 octahedra show a strong distortion [Fig. 2(*b*)] which is reflected by the variation of the Mg–O distances between 2·02 and 2·28 Å. The mean value of 2·13 Å is close to the values found for octahedrally coordinated magnesium in other structures. In addition to the octahedral holes which are occupied by Mg there exists an identical number of similar structural voids. These holes could be filled by shifting the Mg atoms from z to $z+\frac{1}{2}$. The calculated Mg–O distances for this hypothetical arrangment vary between 1·89 and 2·45 Å with a mean value of 2·17 Å.

Each TeO_6 octahedron shares edges with six MgO_6 octahedra but none with other TeO_6 octahedra. The shared edges of the TeO_6 octahedra have somewhat shorter O–O distances (2·60 Å) than the non-shared edges (2·80 Å). This is due to the high-valent tellurium which has the tendency to keep as far as possible from the Mg^{2+} ions.

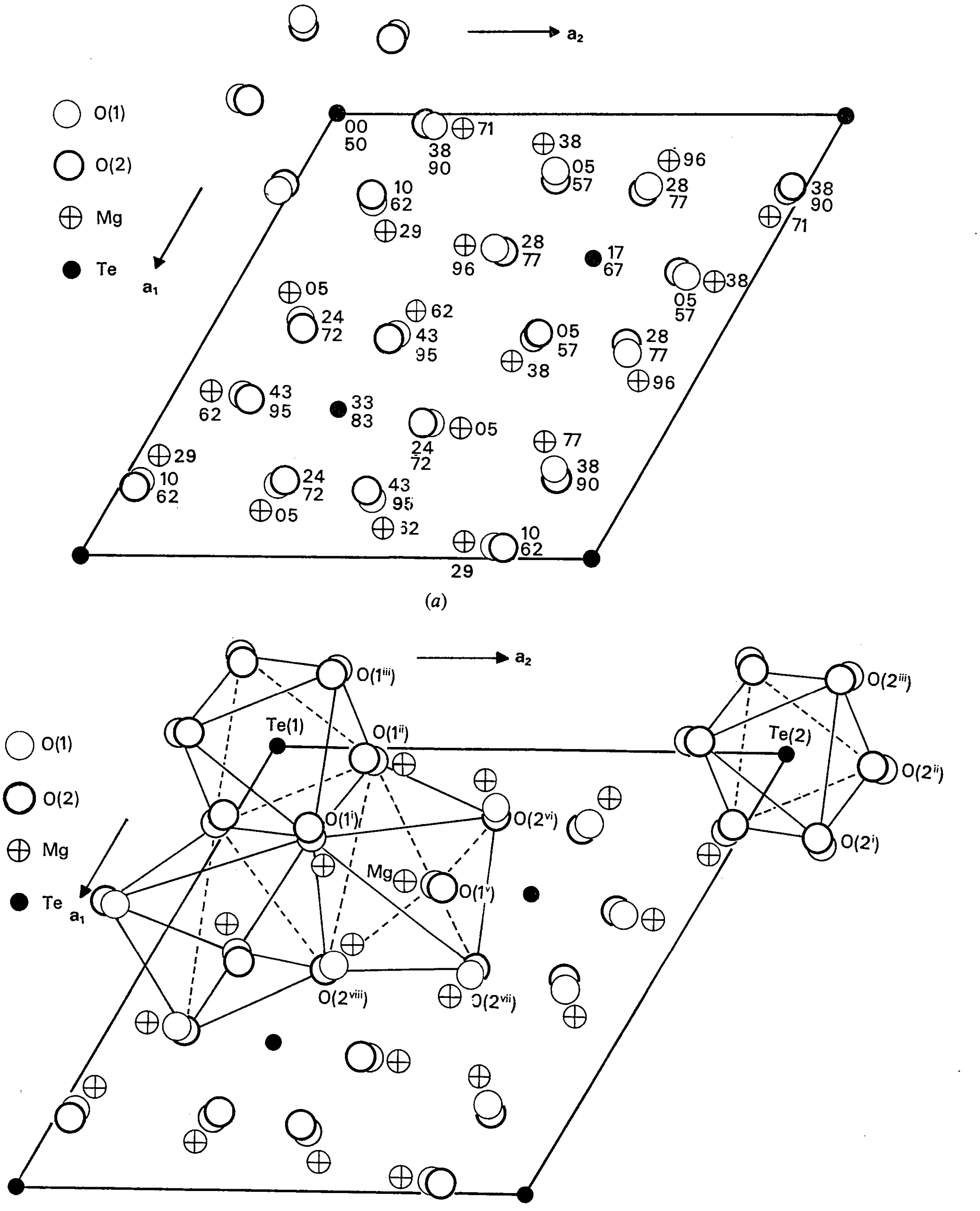
Each of the distorted MgO_6 octahedra shares one edge with a Te(1)O_6 octahedron and another edge with a Te(2)O_6 octahedron, and 4 edges with other MgO_6 octahedra [Fig. 2(*b*)]. The two shortest O–O distances (2·60 Å) of the MgO_6 octahedra correspond to the edges shared with TeO_6 octahedra. The 4 edges which are shared with other MgO_6 octahedra have O–O distances between 2·71 and 2·78 Å. The 6 non-shared edges vary between 3·02–3·66 Å.

Each oxygen is surrounded by one Te^{6+} and three Mg^{2+} ions in the form of a distorted tetrahedron. This satisfies Pauling's second rule, since the charge of O^{2-} is equal to the sum of the electrostatic bond strengths of O–Te and O–Mg: $(6/6+3\times2/6)=2$.

Table 5. Te–O *distances for various compounds*

Compound	Te–O (Å)	Reference
Mg_3TeO_6	1·75	Newnham, Dorrian & Meagher (1970)
Mg_3TeO_6	1·92	Schulz & Bayer (1970)
Cu_3TeO_6	1·908	Hostachy & Coing-Boyat (1968)
Hg_3TeO_6	1·98	Falqui (1963)
$KTeO(OH)_5H_2O$	1·83–1·93	Raman (1964)
$KTeO_2(OH)_3$	1·84–1·89	Lammers & Zemann (1965)
$K_4[Te_2O_6(OH)_4]\ (H_2O)_x$	1·86–2·03	Lindquist & Lundgren (1966)
$Ag_2TeO_2(OH)_4$	1·85–1·997	Fischer (1969)

Table 3 embodies magnitudes and directions of the main axes of the thermal vibration ellipsoids. The small and large main axes of the rotation ellipsoid of the Te atoms are perpendicular and parallel to the *c* axis respectively. The smallest main axis of the Mg atoms is approximately parallel to the direction Mg–O(1^{v}) [*cf.* Fig. 2(*b*)] and nearly perpendicular to the plane O(1^{ii})–O(2^{vi})–O(2^{vii})–O(2^{viii}). This plane contains 4 Mg–O bondings. The intermediate and the largest main axes of the Mg atoms are nearly parallel and perpen-



(*a*)

(*b*)

Fig. 2. (*a*) Projection of the atoms down [0001]. The given numbers are the approximate *z* coordinates. (*b*) Projection of parts of the structure down [0001].

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 ($x \simeq 0\cdot5$). This conclusion was drawn on the basis of X-ray powder diffraction photography with Fe *Kα* 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.