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CRYSTAL STRUCTURES OF THE HIGH PRESSURE POLYMORPHS OF Mn_2GeO_4

NOBUO MORIMOTO, MASAYASU TOKONAMI, KICHIRO KOTO,

AND SHIGEO NAKAJIMA

Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka Japan

ABSTRACT

The crystal structures of two high-pressure polymorphs of Mn_2GeO_4 have been studied in detail with the three-dimensional counter-measured intensities.

The β-phase of Mn_2GeO_4 with the modified spinel structure has the cell dimensions, $a = 6.025$, $b = 12.095$, and $c = 8.752$ Å; $Z = 8$; and the space group *Imma*. The final R is 0.058 for all 522 reflections. This phase is isotypic with the β-phases of Mg_2SiO_4 and Co_2SiO_4. Oxygen atoms form the cubic closest packing arrangement with Mn atoms occupying the octahedral and Ge atoms the tetrahedral cavities as in the spinel structure. However, GeO_4 tetrahedra share one of their oxygen atoms resulting in a Ge_2O_7 group. The average distances of Ge—O and Mn—O are 1.770 and 2.189 Å, respectively. The δ-phase with the Sr_2PbO_4-type structure, described by Wadsley, Reid, and Ringwood (1968), has the cell dimensions $a = 5.257$, $b = 9.270$, and $c = 2.951$ Å and the space group *Pbam*. The final R is 0.053 for all 266 reflections. Ge atoms are in octahedra of oxygen atoms and Mn atoms in polyhedra of seven oxygen atoms. The average Ge—O and Mn—O distances are 1.971 and 2.283 Å, respectively.

INTRODUCTION

Wadsley, Reid, and Ringwood (1968) found that olivine type Mn_2GeO_4 (α-Mn_2GeO_4) transforms to an orthorhombic high pressure form (δ-Mn_2GeO_4) at 120 kbar and 900°C. They determined the crystal structure of δ-Mn_2GeO_4 by the X-ray powder method and confirmed that it is isostructural with Sr_2PbO_4. Morimoto *et al.* (1969) investigated the phase relations of Mn_2GeO_4 at high pressures and high temperatures and found that there is another high pressure polymorph, which is stable over a wide range of temperature and pressure range intermediate between the fields of α-Mn_2GeO_4 and δ-Mn_2GeO_4. Since this polymorph was considered to be isomorphous with the β-phases of $(Mg, Fe)_2SiO_4$ and Co_2SiO_4 described by Ringwood and Major (1966) and Akimoto and Sato (1968), respectively, this polymorph of Mn_2GeO_4 has been called β-Mn_2GeO_4. The stability field of a cubic spinel has not been observed for Mn_2GeO_4 and the densest polymorph was δ-Mn_2GeO_4.

Because the β-phase plays an important role in the high-pressure

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transformations of R_2MX_4 compounds, especially $(Mg, Fe)_2SiO_4$, which is very common in the mantle, the determination of the crystal structure of β-Mn_2GeO_4 was necessary. The transition of the β-phase to the δ-phase in Mn_2GeO_4, instead of the transition to the γ-phase as in $(Mg, Fe)_2SiO_4$, also presented the necessity of structure refinement of δ-Mn_2GeO_4, by which we can increase our understanding of structural relations of R_2MX_4 compounds under high pressures. In this investigation, the crystal structures of the two high-pressure polymorphs of Mn_2GeO_4 have been studied in detail.

Experimental

The cell dimensions, space groups and densities at the atomospheric pressure are given for the three polymorphs of Mn_2GeO_4 (Table 1, Morimoto *et al.*, 1969).

a) β-Mn_2GeO_4

Data Collection. The structure of β-Mn_2GeO_4 has been determined with single crystals synthesized at 1240°C and 64 kbar from α-Mn_2GeO_4. The orthorhombic cell dimensions are compared with those of the β-phase of Mg_2SiO_4 and Co_2SiO_4 (Table 2). The calculated density is 5.13 g.cm^{-3} with the cell content of 8 [Mn_2GeO_4]. The diffraction aspect is *I**a*, giving the possible space groups *Imma, Im2a* and *I2mb*. A nearly spherical crystals of 0.1 mm in diameter was used for collecting intensity data. Three-dimensional intensitie for 522 symmetrically independent reflections were measured by the automatic four-circle diffractometer using Mo$K\alpha$ out to a maximum diffraction range of $\sin\theta/\lambda = 0.72$ by the $\omega - 2\theta$ scan method. Of these reflections, 31 were same as or less than the background value and were regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made.

Structure Determination. Because the cell dimensions of the β-phase for Mg_2SiO_4 and Co_2SiO_4 (Table 2) are obtained by the transformation matrix $\frac{1}{2}\ \frac{1}{2}\ 0/110/001$ from those of the corresponding true spinels (Fig. 1), it is reasonable to assume that oxygen atoms occupy similar positions in both structures with the cubic closest packing. If we assume symmetry centers in the structure of the β-phase, the possible space group is *Imma*. This centrosymmetric space group was adopted during the structure determination and successful refinement of the structure confirmed this choice.

Table 1. Cell dimensions, space group, and density of Mn_2GeO_4 polymorphs.

Polymorph	a (Å)	b (Å)	c (Å)	Space group	Density (g cm^{-3})
α-Mn_2GeO_4	5.061(1)	10.719(1)	6.295(1)	Pbnm	4.79
β-Mn_2GeO_4	6.025(2)	12.095(4)	8.752(2)	Imma	5.13
δ-Mn_2GeO_4	5.262(1)	9.274(4)	2.954(1)	Pbam	5.68

The standard deviations in parentheses are expressed in the unit of the last digit stated.

Table 2. Cell dimensions of the β-phases for three compositions.

Composition	a (Å)	b (Å)	c (Å)	References
Mg_2SiO_4	5.710(4)	11.45(2)	8.248(9)	Ringwood and Major(1966) Akimoto and Sato(1969)
Co_2SiO_4	5.753(1)	11.522(4)	8.337(2)	Akimoto and Sato (1968)
Mn_2GeO_4	6.025(2)	12.095(4)	8.752(2)	Morimoto et al.(1969)

The standard deviations in parentheses are expressed in the unit of the last digit stated.

All computations in the present investigation were carried out on the HITAC 5020E computer of the University of Tokyo using the *UNICS System* (1967). The Patterson projection on (100) of β-Mn_2GeO_4 enabled us to determine the positions of metal atoms; tetrahedral sites (*A* sites) for Ge atoms and octahedral sites (*B* sites) for Mn atoms. The initial parameters of metal atoms determined from the Patterson projection and those of oxygen atoms obtained from the spinel structure were used for the structure factor calculations for *hko* and *okl*. Then the Fourier projections on (001) and (100) were synthesized to obtain the displacements of oxygen and metal atoms from the initial positions. Further

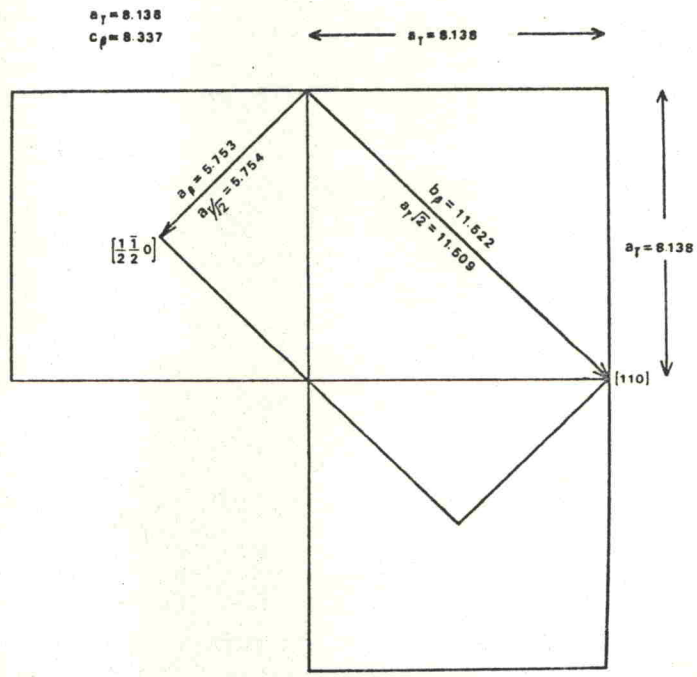


FIG. 1. Relationship of the unit cells of spinal and β-phase. a_γ: the translations of spinel; a_β, b_β, and c_β: the translations of β-phase.

refinements were carried out by the full-matrix least-squares method using the program *ORFLS* of Busing, Martin, and Levy (1962), modified by Sakurai to the *UNICS System* (1967). The function minimized in the refinements was $\Sigma 1/(\sigma)^2 \; ||F_o| - |F_c||^2$, where σ represents the estimated standard deviation computed from counting statistics. Scattering factors and the real and imaginary dispersion corrections for Mn^{2+} and those for Ge^{4+} were taken from International Tables for X-ray Crystallography (1962), while scattering factors for O^{2-} were taken from the values reported by Tokonami (1965). Dispersion corrections for O^{2-} were assumed to be zero.

Three cycles of refinement of the atomic coordinates and one scale factor were made, keeping the isotropic temperature factor $B = 1.0$ for all atoms. In the next three cycles, individual isotropic temperature factors were allowed to vary. The weighted residual R for all 522 reflections reduced to 0.055. Finally the isotropic temperature factors were converted to the anisotropic form and after three cycles of refinement, varying the scale factor, atomic coordinates, and anisotropic temperature factors, no further change of parameters took place. The final residual and weighted residual are 0.058 and 0.030, respectively, for all 522 reflections.

The final parameters, the individual anisotropic temperature factors and the equivalent isotropic temperature factors are listed with their estimated standard deviations (Table 3). F_o and F_c values are on deposit.[1]

b) δ-Mn_2GeO_4

Data Collection. The single crystals used for the structure study were synthesized at 840°C and 64 kbar from α-Mn_2GeO_4. The cell dimensions and space group are compared with other polymorphs (Table 1). A single crystal of approximately hexagonal prism with $0.03 \times 0.03 \times 0.27$ mm^3 size was used for collecting intensity data. Three-dimensional intensities were obtained in the similar procedure as for β-Mn_2GeO_4 described above. Of the observed 266 reflections, 8 were same as or less than the background values and were regarded to be zero in intensity. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made.

Structure Refinement. Structure refinement was initiated using the Wadsley, Reid and Ringwood (1968) atomic coordinates of δ-Mn_2GeO_4 and isotropic temperature factors of 0.5 for Mn and Ge atoms and 1.0 for oxygen atoms. The procedures in the least squares refinement were similar for β-Mn_2GeO_4 described above.

After several cycles of the least squares refinement during which atomic coordinates, isotropic temperature factors, and one scale factor were varied, the R value for 266 reflections reached 0.066. Temperature factors then converted to anisotropic form and four cycles of refinement, varying the scale factor, atomic coordinates and anisotropic temperature factors, further reduced the R value for all reflections to 0.053. The weighted R is 0.039.

The final parameters, the individual anisotropic temperature factors and the

[1] To obtain a copy of this material, order NAPS Document Number 01667 from National Auxiliary Publications Service of the A. S. J. S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC-NAPS.

Table 3. Final atomic coordinates, anisotropic temperature factors, and equivalent isotropic temperature factors for atoms in β-Mn_2GeO_4.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{31}	β_{23}	$\beta_{(equiv.)}$
Mn(1)	0	0	0	0.0045 (10)	0.0007 (2)	0.0022 (4)	0	0	-0.0003 (2)	0.58
Mn(2)	0	1/4	-0.0316 (3)	0.0045 (10)	0.0006 (2)	0.0020 (3)	0	0	0	0.54
Mn(3)	1/4	0.1281 (2)	1/4	0.0031 (5)	0.0009 (1)	0.0023 (2)	0	-0.0003 (2)	0	0.56
Ge	0	0.1192 (1)	0.6164 (2)	0.0030 (3)	0.0006 (1)	0.0014 (1)	0	0	0.0001 (1)	0.40
O(1)	0	1/4	0.2123 (14)	0.0012 (36)	0.0009 (8)	0.0051 (19)	0	0	0	0.75
O(2)	0	1/4	0.7187 (14)	0.0178 (54)	0.0019 (9)	0.0008 (16)	0	0	0	1.31
O(3)	0	-0.0091 (7)	0.2546 (11)	0.0014 (30)	0.0023 (6)	0.0020 (11)	0	0	0.0007 (7)	0.72
O(4)	0.2588 (9)	0.1223 (8)	-0.0034 (6)	0.0084 (15)	0.0013 (3)	0.0023 (6)	0.0006 (13)	-0.0003 (10)	-0.0001 (4)	0.90

The standard deviations, σ, in parentheses are expressed in units of the last digit.

Table 4. Final atomic coordinates, anisotropic temperature factors, and equivalent isotropic temperature factors for atoms in δ-Mn_2GeO_4.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β (equiv.)
Mn	0.0622 (3)	0.3222 (2)	1/2	0.0048 (5)	0.0027 (2)	0.040 (23)	-0.0001 (3)	0.53
Ge	0	0	0	0.0053 (5)	0.0017 (2)	0.033 (21)	0	0.43
O(1)	0.2295 (14)	0.0433 (7)	1/2	0.0078 (25)	0.0026 (9)	0.029 (88)	-0.0019 (13)	0.62
O(2)	0.3722 (13)	0.3141 (8)	0	0.0066 (24)	0.0017 (8)	0.030 (89)	0.0000 (12)	0.47

The standard deviations, σ, in parentheses are expressed in units of the last digit stated.

equivalent isotropic temperature factors are listed with their estimated standard deviations (Table 4). F_o and F_c values are on deposit.[1]

Discussion of the Structures

The bond distances and angles were computed for the two polymorphs of Mn_2GeO_4 using Sakurai's program of the *UNICS System* (1967), RSDA-4 (Tables 5 and 6). The standard deviations of the atomic coordinates were used to compute the errors in the distances and angles.

a) β-Mn_2GeO_4

The structure of β-Mn_2GeO_4 is projected on (001) (Fig. 2). The oxygen atoms build approximately the cubic closest packing as in spinel. Although Ge atoms occupy the tetrahedral A sites and Mn atoms, the octahedral B sites in both structure, the arrangements of A and B sites in β-Mn_2GeO_4 are different from those in spinel. For comparison, the structure of spinel, with R_2MX_4 composition, is shown (Fig. 2), where the M atoms are at the A sites and the R atoms at the B sites. Two GeO_4 tetrahedra, which would be isolated in the spinel structure, share one of their oxygen atoms resulting in a Ge_2O_7 group and an oxygen atom not bonded to any Ge atom. Thus in order to obtain the structure of the β-phase, we must modify the spinel structure by displacing four M and four R atoms out of the eight M and sixteen R atoms in the cell.

[1] To obtain a copy, see footnote on p. 65.

Table 5. Interatomic distances and angles in β-Mn_2GeO_4

Ge_2O_7 group:		$Mn(2)O_6$ octahedron:	
Ge-O(2)	1.817(6) Å ×1*	Mn(2)-O(1)	2.134(13) Å ×1
-O(3)	1.746(9) ×1	-O(2)	2.186(13) ×1
-O(4)	1.758(6) ×2	-O(4)	2.208(8) ×4
Mean	1.770	Mean	2.192
O(2)-O(3)	2.923(8) Å ×1	O(1)-O(4)	2.895(11) Å ×4
O(2)-O(4)	2.836(11) ×2	O(2)-O(4)	3.276(11) ×4
O(3)-O(4)	2.911(11) ×2	O(4)-O(4)'	3.088(8) ×2
O(4)-O(4)	2.907(8) ×1	O(4)'-O(4)"	3.118(8) ×2
Mean	2.887	Mean	3.078
O(2)-Ge-O(3)	110.22(25)° ×1	O(1)-Mn(2)-O(4)	83.59(15)° ×4
O(2)-Ge-O(4)	104.97(33) ×2	O(2)-Mn(2)-O(4)	96.41(16) ×4
O(3)-Ge-O(4)	112.33(30) ×2	O(4)-Mn(2)-O(4)'	88.74(27) ×2
O(4)-Ge-O(4)	111.50(25) ×1	O(4)'-Mn(2)-O(4)"	89.84(27) ×2
Mean	109.39	Mean	89.76
$Mn(1)O_6$ octahedron:		$Mn(3)O_6$ octahedron:	
Mn(1)-O(3)	2.231(10) Å ×2*	Mn(3)-O(1)	2.134(3) Å ×2
-O(4)	2.150(8) ×4	-O(3)	2.241(6) ×2
		-O(4)	2.220(5) ×2
Mean	2.177	Mean	2.198
O(3)-O(4)	3.172(11) Å ×4	O(1)-O(1)	3.084(4) Å ×1
O(3)-O(4)"	3.023(10) ×4	O(1)-O(3)	3.156(9) ×2
O(4)-O(4)'	3.118(8) ×2	O(1)-O(4)	2.895(11) ×2
O(4)'-O(4)"	2.960(13) ×2	O(1)-O(4)'	3.315(11) ×2
		O(3)-O(3)	3.014(1) ×1
Mean	3.078	O(3)-O(4)	3.062(11) ×2
		O(3)-O(4)'	3.172(11) ×2
O(3)-Mn(1)-O(4)	92.75(19)° ×4		
O(3)-Mn(1)-O(4)'	87.25(19) ×4	Mean	3.110
O(4)-Mn(1)-O(4)'	92.98(28) ×2		
O(4)-Mn(1)-O(4)"	87.02(28) ×2	O(1)-Mn(3)-O(1)	92.56(11)° ×1
		O(1)-Mn(3)-O(3)	92.29(14) ×2
Mean	90.00	O(1)-Mn(3)-O(4)	83.33(32) ×2
		O(1)-Mn(3)-O(4)	99.17(38) ×2
		O(3)-Mn(3)-O(3)	84.48(21) ×1
		O(3)-Mn(4)-O(4)	86.73(32) ×2
		O(3)-Mn(3)-O(4)	90.62(32) ×2
		Mean	90.11

* Number of equivalent distances or angles in the tetrahedron and octahedron

The standard deviations in parentheses are expressed in units of the last digit stated.

Both spinel and β-phase are considered to be built of a series of layer (Fig. 3). Figures 3a and b represent the consecutive layers of the spinel structure and show diagonal chains of the *B* octahedra. The orientations of the chains are perpendicular in the consecutive layers. Thus the spinel structure can be characterized by a three-dimensional framework of the chains of octahedra running parallel to the six face diagonals of the cubic cell. Figures 4a and b represent the consecutive layers of β-Mn_2GeO_4, in which double chains of the *B* octahedra are characteristic. Furthermore, straight chains run only parallel to the *a* and *b* axes, corresponding to the diagonals of one of the three faces of the cubic spinel cell (Tokonami *et al.*, in press).

It is of interest to notice that O(1) is not bonded to any Ge atom

Table 6. Interatomic distances and angles in β-Mn_2GeO_4

GeO_6 octahedron:		MnO_7 polyhedron:	
Ge-O(1)	1.950(5) Å ×4*	Mn-O(1)	2.732(7) Å ×1*
-O(2)	1.851(7) ×2	Mn-O(1)'	2.325(8) ×1
		O(1)"	2.149(3) ×1
Mean	1.917	O(2)	2.202(6) ×2
		O(2)'	2.186(6) ×2
O(1)-O(1)'	2.546(10) Å ×2		
O(1)'-O(1)"	2.954(1) ×2	Mean	2.283
O(1)-O(2)	2.733(9) ×4		
O(1)'-O(2)	2.644(9) ×4	O(1)-O(2)	3.008(9) ×2
		O(1)-O(2)'	2.733(9) ×2
Mean	2.705	O(1)'-O(1)"	2.957(11) ×1
		O(1)'-O(2)	2.644(9) ×2
O(1)-Ge-O(1)'	81.51(22)° ×2	O(1)"-O(2)'	3.008(9) ×2
O(1)'-Ge-O(1)"	98.49(23) ×2	O(2)-O(2)'	2.887(10) ×2
O(1)-Ge-O(2)	91.90(24) ×4	O(2)-O(2)"'	2.954(1) ×2
O(1)'-Ge-O(2)	88.10(24) ×4		
		Mean	2.879
Mean	90.00		
		O(1)-Mn-O(2)	74.27(22)° ×2
		O(1)-Mn-O(2)'	66.44(21) ×2
		O(1)'-Mn-O(1)"	85.03(18) ×2
		O(1)'-Mn-O(2)	71.39(22) ×2
		O(1)"-Mn-O(2)'	87.88(23) ×2
		O(2)-Mn-O(2)'	82.29(21) ×2
		O(2)-Mn-O(2)"'	84.26(17) ×1
		O(2)'-Mn-O(2)"	85.03(18) ×1

* number of equivalent distances or angles in the octahedron and polyhedron

The standard deviations in parentheses are expressed in units of the last digit stated.

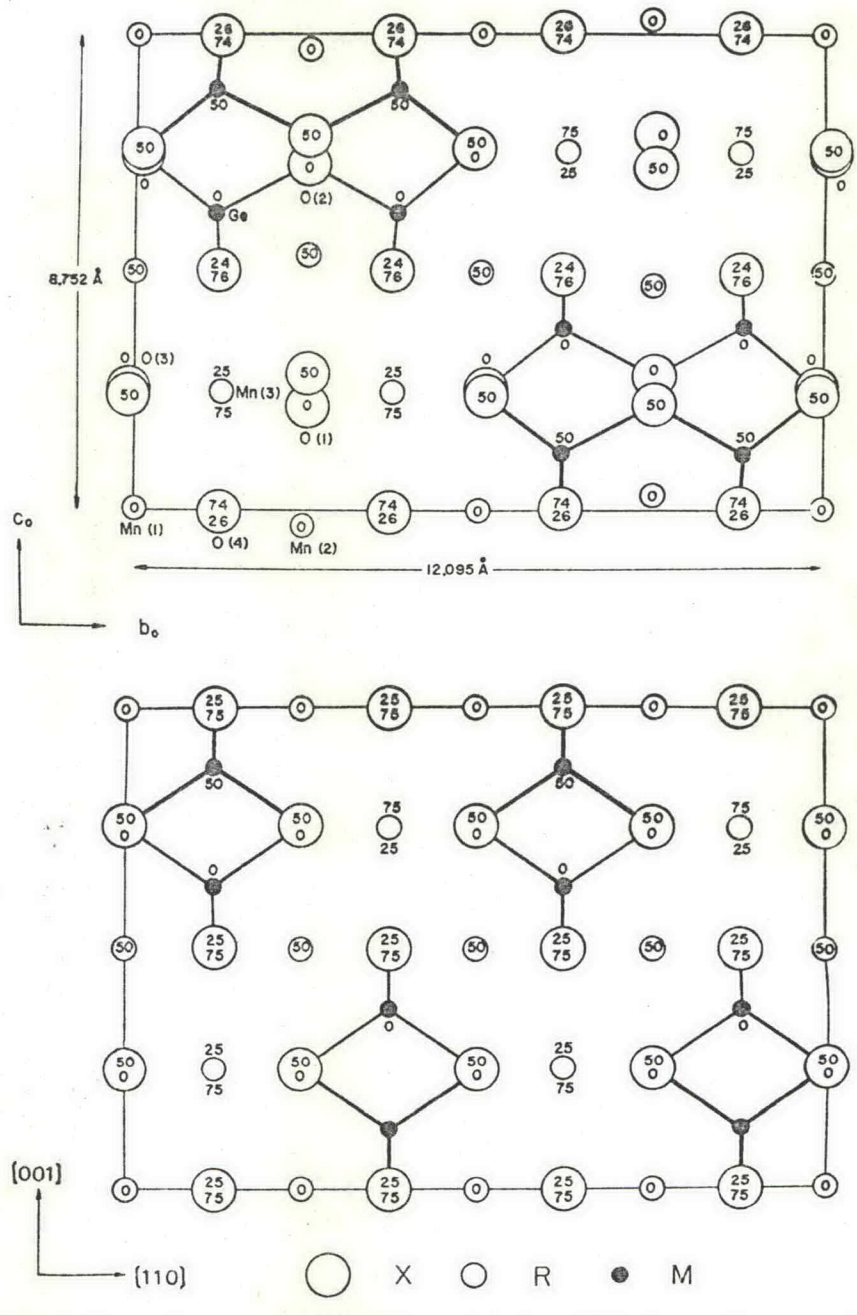


FIG. 2. Upper: Structure of β-Mn_2GeO_4, projected on (001). Lower: Structure of spinel, R_2MX_4, projected on $(1\bar{1}0)$.

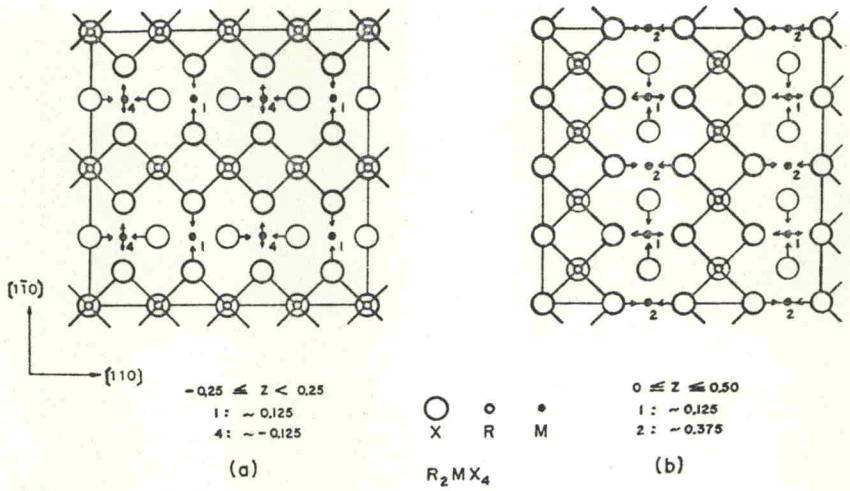


FIG. 3. Chains of the octahedra in the spinel structure.

but to five Mn atoms, and that O(2) is bonded to two Ge atoms and one Mn atom, because of the formation of the Ge_2O_7 groups. O(3) and O(4) are bonded to one Ge atom and three Mn atoms. The Ge—O distances of the tetrahedra range from 1.746 to 1.817 Å with the mean value of 1.770 Å. The Ge_2O_7 group is schematically shown with the bond distances and angles in Figure 5. The bridging Ge—O bonds are definitely longer than the nonbridging bonds. The Mn—O distances

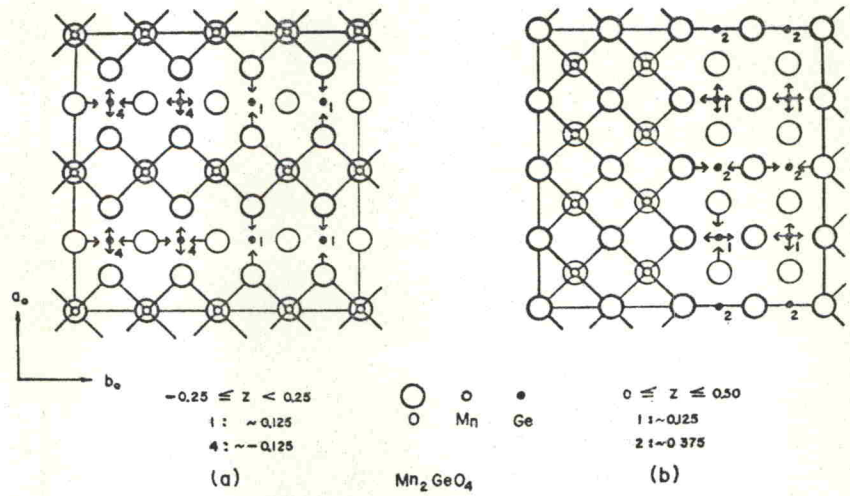


FIG. 4. Double chains of the Mn-octahedra in β-Mn_2GeO_4.

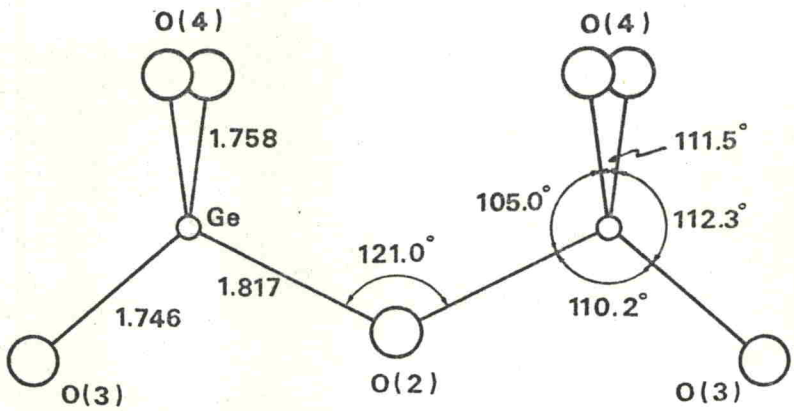


FIG. 5. Ge_2O_7 group in β-Mn_2GeO_4.

of the octahedra are from 2.134 to 2.241 Å with the mean value of 2.198 Å (Table 5).

The interatomic distances and angles in β-Mn_2GeO_4 can be compared with those in manganese metagermanate, $MnGeO_3$ (Fang, Townes, and Robinson, 1969), which is isotypic with enstatite. Average

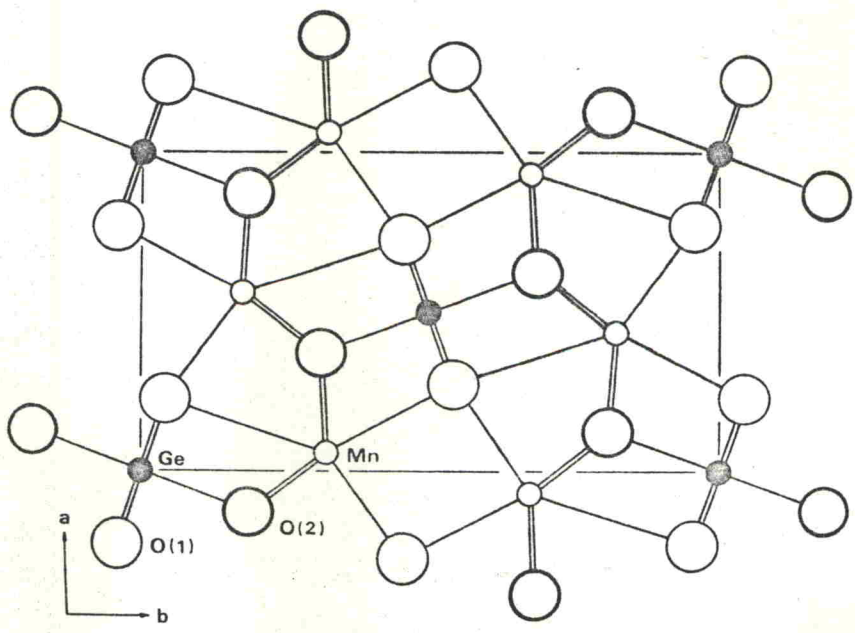


FIG. 6. Structure of δ-Mn_2GeO_4, projected on (001).

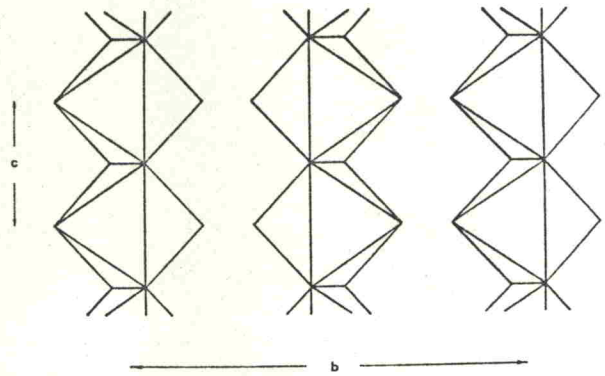


FIG. 7. Chain structure of the Ge-octahedra in δ-Mn_2GeO_4.

Ge—O and Mn—O distances are 1.75 Å and 2.21 Å, respectively, in this structure.

b) δ-Mn_2GeO_4

The structure of δ-Mn_2GeO_4 is projected on (001) (Fig. 6). The octahedral coordination of oxygen atoms around Ge atoms is characteristic in this structure. The germanium-oxygen octahedra make chains running parallel to the *c*-axis, which are seen end on in the projection at the corners and center of the unit cell. In these chains,

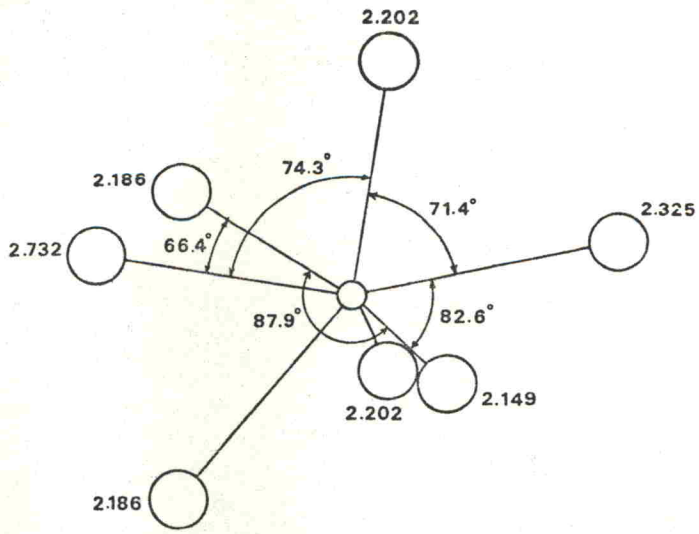


FIG. 8. Coordination of oxygen atoms around Mn^{2+} in δ-Mn_2GeO_4.

each octahedron shares an edge with a neighbouring octahedron on either side (Fig. 7). The chains are linked sideways by coordination polyhedra around Mn atoms. Wadsley *et al.* (1968) considered that Mn^{2+} has six oxygen atoms at the corners of a somewhat distorted trigonal prism. However, the central Mn atom is very close to one of the faces and the seventh oxygen atom is at a distance of 2.732 Å from the Mn atom, and is considered to be bonded to the central Mn atom (Fig. 8). The oxygen-oxygen distances in the polyhedra around Mn atom (Table 6) seem to support this coordination.

c) *Stability of the polymorphs*

In the structure of β-Mn_2GeO_4, Pauling's electrostatic balance rule fails for O(1) and O(2), the charge balance being $-1/3$ for O(1) and $+1/3$ for O(2). The negative charge on O(1), responsible for short distances of this oxygen to Mn atoms, compensates for the surplus charge of O(2), in the form of long distances of this oxygen to Ge and Mn atoms. In the structure of δ-Mn_2GeO_4, the rule is satisfied if the Mn atoms are considered to be coordinated only by six oxygen atoms forming the trigonal prism. However, if the seventh oxygen is added into coordination around the Mn atom as we have previously discussed, the rule is not completely satisfied.

A structure of hypothetical γ-Mn_2GeO_4 can be built on the assumption that the relations between the structures of β-, and γ-Co_2SiO_4 can be applied on those between the structures of β-, and γ-Mn_2GeO_4 (Tokonami *et al.*, in press). Thus the Ge—O and Mn—O distances would be equal in this hypothetical structure with the corresponding average distances in the β-phase (1.77 Å and 2.19 Å, respectively). Although this hypothetical structure satisfies the Pauling's rule, we can not find any stability field of γ-Mn_2GeO_4 in the phase diagram. This indicates that γ-Mn_2GeO_4 is less stable than β-Mn_2GeO_4 at relatively high pressures and less stable than γ-Mn_2GeO_4 at high pressures. The relative stability between these three polymorphs will be discussed in more detail later.

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