

are smaller, and those around C(5)–O(5) and O(5)–C(1) are larger, *i.e.*, 35.1, 35.1 and 75.3, 75.8° respectively. There are corresponding differences in the deviations of C(3) and O(5) from the plane of C(1), C(2), C(4), C(5) (Table 5). The angle at the pyranose ring oxygen, O(5), is about 10° smaller than normal and comparable with that at the oxygen in the anhydro ring.

The hydrogen bonding is shown in Table 6 and Fig. 5(a) and (b). The hydroxyls at O(2) and O(4) form two hydrogen bonds, one donor and one acceptor; that at O(3) forms only a donor bond to O(2). The molecules are linked by finite chains of hydrogen bonds through O(3b)H–O(2)H–O(4c)H–O(1d). The hydrogen H(O2) is 'anti' to H(2) with respect to the C(2)–O(2) bond and O(2)–H(O2) is directed toward the mid-point of the triangle formed by O(5) and O(4) of the same molecule and O(4c) of an adjacent molecule. The distances from H(O2) to O(4c), O(5) and O(4) are 1.86, 2.57 and 2.98 Å. Therefore, only the intermolecular interaction can be regarded as a hydrogen bond. However, there is nuclear magnetic resonance and infrared spectral evidence that this 'anti' conformation of H(O2) occurs in a 5% CCl₄ solution of the 3,4-dimethyl ether derivative and that this may be a characteristic 'conformational' property of certain levoglucosan derivatives (Seib, 1970). This would imply some intramolecular stabilization of the conformation observed in this structure.

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The Crystal Structure of the ν Phase, Mn_{81.5}Si_{18.5}*

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The crystal structure of the ν phase, Mn_{81.5}Si_{18.5} has been determined by single-crystal X-ray diffraction analysis. The lattice constants are $a_0 = 16.992$ (4), $b_0 = 28.634$ (7), $c_0 = 4.656$ (1) Å, and the space group is *Immm* (D_{2h}^{25}), with 186 atoms in the unit cell. The structure has been refined by full-matrix least-squares analysis to a final *R* index of 0.041, based on the 2305 reflections observed with the diffractometer. The ν phase is related to the *P* phase, and belongs to the family of σ -phase related, layered, tetrahedrally close-packed structures, with percentages of sites with CN 12, 14, 15 and 16 respectively: 40, 43, 11 and 6. All positions with CN > 12 are occupied by Mn, except two CN 14 positions which have some Si present. The CN 12 positions are occupied by various mixtures of Mn and Si, except three positions which are occupied by Mn only, and two positions which are occupied by Si only. The structure may also be described as a stacking of two kinds of 'tiles' each consisting of 7 hexagons and 12 triangles, with the space in-between filled up by hexagons, pentagons and triangles.

Introduction

The ν phase was described by Gupta (1964) in the Mn–Fe–Si system as a binary Mn–Si phase about one

at. % wide, centered at 81.5 at. % Mn and extending into the ternary system only up to 1.5 at. % Fe. Earlier the occurrence of a complex phase in the Mn–Si system in this region was mentioned by Åmark, Borén & Westgren (1936) and subsequently called the *N* phase by Kuzma & Hladyshevskii (1964). A specimen of the ν phase of stated composition Mn_{81.5}Si_{18.5}, annealed for 72 hours at 1000°C, was kindly made available to us

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by Professor Paul A. Beck for single-crystal study. No chemical analysis of the alloy was made; weight loss due to annealing and melting had been found to be less than 1%.

Experimental

Intensity data for a crystal fragment in arbitrary orientation were collected by Dr A. S. Parkes of the Chemistry Department of M.I.T. on a Datex-automated four-circle General Electric diffractometer with Mo $K\alpha$ radiation. A θ - 2θ scan was used and 3373 independent reflections were recorded out to $2\theta = 75^\circ$. The scan rate was 1 deg. min^{-1} ; the 2θ range was 1.4° plus the α_1 , α_2 angular separation. Background readings were made at the end of each scan range for 20 seconds. The 2305 reflections larger than 3σ above the background were used in the crystal structure determination.

The cell dimensions, as refined from diffractometer measurements by least squares are:

$$a_0 = 16.992 \text{ (4)}, \quad b_0 = 28.634 \text{ (7)}, \quad c_0 = 4.6556 \text{ (14) \AA}.$$

There were no systematic extinctions other than those for body-centering. Possible space groups are: $I222$ (D_2^3), $I2_12_12_1$ (D_2^5), $Imm2$ ($I2mm$, $Im2m$) (C_{2v}^{20}) and $Immm$ (D_{2h}^{25}). The density, measured with a pycnometer, is 7.01 (10) g. cm^{-3} and the calculated number of atoms per unit cell is 193 (3). The crystal fragment was irregularly shaped with dimensions varying between 0.0043 and 0.0126 cm. An absorption correction with $\mu = 215 \text{ cm}^{-1}$ was applied later in the analysis by the method and computer program described by Wuensch & Prewitt (1965), with the shape of the crystal approximated by seven faces and with 68 integration points. The correction factor applied to the intensities varied between 4.167 and 1.961 . In a later stage of the refinement a secondary extinction correction was applied.

Trial structure

The diffraction pattern of the ν phase shows a concentration of high intensities in shells in reciprocal space at about $1/d = 0.48$, 0.90 and 1.44 \AA^{-1} , separated by shells of low intensity, a feature characteristic of tetrahedrally close-packed structures (Shoemaker & Shoemaker, 1969). The intensities of layer lines $l \pm 4$ are equal to the corresponding ones for layer lines l (except for normal decline) indicating that the atoms are confined to layers parallel to (001) planes, quartering the cell, as in the layered tetrahedrally close-packed structures. The diffraction pattern has a strong pseudo-hexagonal character and shows some resemblance with the diffraction pattern of the P phase (Shoemaker, Shoemaker & Wilson, 1957) after rotating about the z axis by approximately 15° . The cell volume of the ν phase is about three times as large as that of the P phase. Three trial structures were derived in space group $Immm$, with similar projections down the z axis, but differing in the arrangement of the secondary atoms (the atoms between the mirror planes perpendicular to

the z axis, which contain the main layers). All three structures had 186 atoms per unit cell, but differed in the ratios of CN 16, 15, 14, and 12 atoms. The selection of the correct structure was made on the basis of least-squares cycles using low-order structure factors with $l = 0, 1, 2$.

Refinement of the structure

The trial structure was refined by full-matrix least-squares analysis with the program *ORFLS* (Busing, Martin & Levy, 1962) as modified by Stewart & Kundell and incorporated in the program system *X-ray 67* (1967). The Mn atoms were assumed to occupy the CN 14, 15 and 16 positions and the Si atoms with the remaining Mn atoms were assumed to be uniformly distributed among the CN 12 positions. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and corrected for the real part of the anomalous dispersion (Cromer, 1965) with $\Delta f'$ taken as 0.36 for Mn and 0.09 for Si. The function minimized was $\sum w(F_o - F_c)^2$. The weights were based on the standard errors in F_o assuming $\sigma(I_o) = [\sigma_c^2 + (0.05 I_o)^2]^{1/2}$ where I_o is the observed uncorrected intensity and σ_c is the standard error in the intensity based on the counting statistics. At the start 40 parameters were varied: one scale factor and 39 positional parameters, keeping constant all isotropic temperature factors and the z parameters of the secondary atoms. The refinement using all reflections with $l \leq 2$ became very slow at $R = 0.34$. At this point a preliminary 'refinement' (without recourse to the intensity data) was made by adjusting the parameters by least-squares to fit the distances to the values predicted on the basis of the coordination numbers of the atoms, the type of the ligands and the average CN 12 radius of the atoms (Shoemaker & Shoemaker, 1964). After four more conventional least-squares cycles on a limited set of $hk0$ data, the R value for all data with $l \leq 2$ dropped to 0.18 . An attempt to vary isotropic temperature factors resulted in negative values for several atoms and an absorption correction was applied (see *Experimental*). Four cycles in which the scale factor, positional parameters and isotropic temperature factors were varied decreased R to 0.08 with negative temperature factors for three CN 12 atoms. The variation of the temperature factors for the CN 12 positions seemed to indicate that the assumed occupancy of these sites with the same mixture of Mn and Si was not correct. One cycle in which the occupancies and the positional coordinates were varied with B held constant at an average value for each type of atom, resulted in an R value for all reflections with $l \leq 2$ of 0.052 and occupancies that indicated that three CN 12 positions were almost entirely occupied by Mn and two almost entirely by Si. From this point on all 2305 observed reflections were used in the refinement and a correction for secondary extinction was applied to the 50 largest structure factors of the form $F_o^{\text{corr}} = F_o(1 + gI_o)$ with $g = 1.33 \times 10^{-5}$ (Zachariasen, 1963).

Table 1. Atomic parameters for the ν phase

		The B values (\AA^2) listed are those for the temperature factor expression: $\exp[-\frac{1}{4}(a_1^2 B_{11} h^2 + \dots + 2a_1 a_2 B_{12} hk + \dots)]$.											f_0	$\% \text{Mn}$
CN	Atom	Site	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}			
14	Mn(1)	8(n)	0.35291 (5)	0.07262 (3)	0	0.54 (3)	0.48 (3)	0.66 (4)	0.04 (2)			25.5 (2)	100.0	
14	Mn(2)	8(n)	0.27979 (5)	0.14505 (3)	0	0.57 (3)	0.41 (3)	0.65 (4)	-0.03 (2)			25.5 (2)	100.0	
14	Mn(4)	8(n)	0.07025 (5)	0.22005 (4)	0	0.57 (3)	0.56 (3)	0.60 (3)	-0.09 (2)			25.5 (2)	100.0	
14	Mn(5)	16(o)	0.36581 (4)	0.36105 (2)	0.24703 (16)	0.66 (2)	0.72 (2)	0.48 (2)	0.03 (2)	-0.01 (2)	-0.12 (2)	25.6 (1)	100.0	
14	Mn(13)	8(n)	0.11799 (6)	0.37155 (3)	0	0.63 (3)	0.41 (3)	0.64 (4)	-0.03 (2)			25.3 (2)	100.0	
14	Mn(16)	8(m)	0.23201 (5)	$\frac{1}{2}$	0.24648 (22)	0.66 (3)	0.56 (3)	0.42 (3)		-0.08 (2)	0.05 (3)	24.3 (2)	90.5	
14	MnSi(24)	8(l)	0	0.42061 (4)	0.25332 (24)	0.61 (3)	0.71 (3)	0.47 (4)				21.9 (2)	69.4	
14	MnSi(26)	4(i)	0	0	0.26250 (37)	0.56 (5)	0.53 (5)	0.47 (6)	-0.04 (2)			25.3 (2)	100.0	
14	Mn(28)	8(n)	0.24397 (6)	0.41106 (3)	0	0.54 (3)	0.52 (3)	0.61 (4)				25.8 (2)	100.0	
14	Mn(29)	4(h)	$\frac{1}{2}$	0.32107 (5)	0	0.71 (4)	0.48 (4)	0.62 (5)				24.9 (2)	100.0	
15	Mn(6)	8(n)	0.36892 (6)	0.45478 (4)	0	0.57 (3)	0.45 (3)	0.58 (4)	-0.02 (2)			25.9 (2)	100.0	
15	Mn(18)	4(e)	0.42673 (8)	0	0	0.65 (4)	0.54 (4)	0.61 (5)				25.0 (2)	100.0	
15	Mn(20)	4(h)	$\frac{1}{2}$	0.40817 (5)	0	0.62 (4)	0.45 (5)	0.59 (5)				25.5 (2)	100.0	
15	Mn(21)	4(h)	$\frac{1}{2}$	0.23281 (5)	0	0.58 (4)	0.51 (5)	0.78 (5)				25.0 (2)	100.0	
16	Mn(12)	8(n)	0.22534 (6)	0.22751 (4)	0	0.60 (3)	0.63 (3)	0.66 (4)	0.18 (2)			25.0 (2)	100.0	
16	Mn(22)	4(g)	0	0.31376 (5)	0	0.51 (4)	0.82 (5)	0.63 (5)				20.8 (2)	59.1	
12	MnSi(3)	8(n)	0.43143 (7)	0.14709 (4)	0	0.50 (4)	0.42 (4)	0.58 (4)	0.09 (3)			19.6 (2)	49.1	
12	MnSi(8)	8(m)	0.24733 (7)	0.32296 (4)	0	0.42 (4)	0.37 (4)	0.52 (5)	-0.01 (3)			19.8 (2)	50.2	
12	MnSi(9)	8(m)	0.36744 (7)	0.28168 (5)	0	0.60 (4)	0.39 (4)	0.55 (5)	0.08 (3)			17.5 (2)	30.2	
12	MnSi(10)	8(m)	0.11874 (8)	0.45757 (5)	0	0.42 (4)	0.28 (4)	0.54 (5)	-0.08 (3)			25.3 (2)	100.0	
12	Mn(11)	8(n)	0.06744 (5)	0.07019 (3)	0	0.43 (3)	0.43 (3)	0.57 (3)	0.03 (2)			22.5 (1)	75.0	
12	MnSi(14)	16(o)	0.36569 (4)	0.20909 (3)	0.25156 (17)	0.49 (2)	0.40 (2)	0.41 (3)	0.00 (2)	0.03 (2)	-0.01 (2)	13.6 (2)	0.0	
12	Si(15)	8(o)	0.20780 (10)	0.07125 (7)	0	0.23 (6)	0.19 (6)	0.67 (7)	0.03 (4)			25.2 (2)	100.0	
12	Mn(19)	4(e)	0.13492 (8)	0	0	0.47 (4)	0.33 (4)	0.54 (5)				13.6 (2)	0.0	
12	Si(23)	4(g)	0	0.14441 (9)	0	0.23 (8)	0.26 (9)	0.31 (9)				25.4 (2)	100.0	
12	Mn(25)	2(d)	0	$\frac{1}{2}$	0	0.35 (6)	0.47 (6)	0.66 (7)						

With 96 parameters varied (individual isotropic B, positional parameters and occupancies) the R value came down to 0.047, and the final R value after introduction of anisotropic temperature factors (total of 169 parameters) was 0.041. The R-value ratio of 1.14 indicates that this is a significant improvement at the 0.001 significance level (ratio: 1.03).

The final parameters and their standard deviations are listed in Table 1. The values listed under f_0 are the refined scattering factors at $2\theta=0$, derived from the refined occupancies. The last column gives the estimated % Mn, taking into account that f_0 for Mn is 25.36 and for Si is 14.09. The observed and calculated structure factors are in given Table 2. The values entered in the F_0

Table 2. Observed (left column) and calculated (right column) structure factors for the ν phase

Asterisks indicate non-observed reflections (see text); U's indicate reflections obscured by white radiation streaks. Miller indices (HKL) are given for the first (top) reflection in each row; for subsequent reflections k steps by +2.

Table with multiple columns containing Miller indices (HKL) and numerical values for observed and calculated structure factors. The table is organized into several sections based on the Miller index ranges.

Table 2 (cont.)

404	-112	200	51	79	44	151	-104	200	7	58	72	290	19	200	-7	91	-40	270	9	
110	111	300	30	77	72	240	-110	270	40	MEL 15 0 6	41*	10	200	3	170	-110	200	-1		
207	-211	170	-8	68	50	271	104	111	-120	140	100	-42	170	-40	MEL 7 0 7	101	-111	200	-3	
310	-10	170	-10	114	-108	101	163	MEL 13 1 0	200	15	200	250	75	-70	101	-111	200	-30		
95	30	90	92	00	-40	70	37	40	-20	40	50	MEL 1 0 7	MEL 1 0 7	MEL 1 0 7	MEL 1 0 7	MEL 1 0 7	MEL 1 0 7	MEL 1 0 7	MEL 1 0 7	
97	30	67	66	MEL 8 0 6	207	-102	220	-27	350	33	300	25	300	-20	105	-100	MEL 11 0 7	112	-107	
150	-167	600	37	214	-15	210	12	40	-20	470	300	25	300	18	350	340	MEL 11 0 7	112	-107	
154	-311	170	-11	210	17	220	34	80	-40	410	32	250	9	60	41	237	230	200	-4	
250	-270	111	210	5	300	-40	50	-10	170	-100	250	0	50	40	-10	-15	180	15		
300	-310	300	30	170	-18	100	110	200	-50	190	10	300	12	300	12	300	12	300	12	
100	-120	MEL 0 0	103	-90	92	280	-22	40	31	430	-55	300	10	100	-301	240	15	50	40	
200	10	200	200	170	-11	65	107	80	MEL 17 1 0	80	50	370	-41	110	100	100	-40	100	-40	
200	10	200	10	200	11	110	-100	45	-53	410	30	90	95	410	-42	107	-105	70	-55	
270	17	30	81	200	11	430	-60	MEL 17 1 0	80	50	370	-41	110	100	100	-40	100	-40		
60	-31	170	100	430	-60	MEL 17 1 0	80	50	370	-41	110	100	100	-40	100	-40	100	-40		
MEL 0 0 6	70	70	250	-5	50	35	162	147	57	-54	83	-80	71	90	MEL 8 1 7	90	77	70	-97	
112	110	210	4	10	-41	100	-100	MEL 19 0 6	41	-80	100	-80	300	30	241	-231	MEL 12 1 7	10	77	
403	400	51	41	52	-75	552	-467	140	142	260	-27	MEL 2 1 7	MEL 5 0 7	112	90	270	5	67	70	
113	-211	210	27	222	210	157	160	200	0	700	400	11	400	-27	210	2	210	2	210	2
81	67	170	-180	330	25	200	-280	120	115	140	148	300	14	250	15	132	125	270	35	
300	-27	135	135	300	11	250	-25	350	-35	MEL 10 0 6	100	-10	800	65	800	70	270	40		
210	-27	77	70	200	-237	220	10	100	-22	221	111	410	-22	210	18	310	-4	270	40	
200	-65	60	70	MEL 9 1 6	210	21	71	-75	200	-2 0 6	100	10	320	-30	300	10	210	20	210	20
200	-12	700	-227	300	26	220	-237	90	90	107	-100	250	12	50	44	290	27	MEL 13 0 7	13	0 7
170	-170	210	-210	70	70	301	-310	112	110	50	50	210	31	600	-47	210	27	MEL 13 0 7	13	0 7
210	-210	45	50	200	41	210	17	200	10	97	90	40	-20	330	20	300	27	100	-107	
310	0	65	-57	110	-110	300	-40	140	-140	110	-110	310	-12	170	4	MEL 9 0 7	65	-59	110	107
50	50	80	75	310	32	185	-175	300	-23	MEL 12 1 6	270	30	42	43	77	60	65	-59	110	107
200	-200	MEL 7 1 6	150	155	MEL 12 1 6	300	13	270	-11	300	-20	300	40	50	50	300	-50	110	107	
300	-107	50	-137	110	121	133	130	MEL 15 1 6	60	-90	300	42	MEL 6 1 7	60	50	300	-50	110	107	
200	-111	71	-68	100	-100	222	-222	31	50	MEL 0 1 9	MEL 5 0 7	210	-41	50	67	65	65	875	800	800
170	-15	52	51	100	-77	80	-81	200	-35	41	31	200	20	30	65	65	65	875	800	800
MEL 5 1 6	110	-80	70	73	50	70	210	-27	200	17	200	27	30	65	65	65	875	800	800	800
120	115	44	-42	170	-32	320	-310	410	-30	45	40	200	20	60	-30	300	15	110	110	110
200	-17	90	90	50	20	100	10	50	80	30	200	-17	60	-30	300	15	110	110	110	110
205	-207	171	-124	81	70	65	45	51	41	101	101	100	-17	60	-30	300	15	110	110	110
120	111	100	-100	80	40	10	32	50	-73	130	-130	200	-18	60	-30	300	15	110	110	110
50	-57	270	-270	MEL 10 0 6	400	-50	71	-600	300	100	100	100	100	170	-170	100	100	100	100	100
330	19	225	225	MEL 10 0 6	41	-40	140	110	100	250	90	95	300	-2	230	-18	100	100	100	100

column for the non-observed reflections ($< 3\sigma$ above the background) are either derived from the actual count or, in cases where the count was less than the background, approximately $\frac{1}{2} F_{\min}$. No absorption correction was applied to the non-observed reflections and a constant scale factor was used instead. The good

agreement obtained in this structure determination was assumed to indicate that the space group *Immm* was the correct one and therefore the lower symmetrical space groups were not considered.

Description of the structure

Fig. 1 shows a little more than one quarter of the contents of the unit cell of the ν phase as produced by the computer program *ORTEP* (Johnson, 1965). The atoms in the mirror planes at $z=0$ and $z=\frac{1}{2}$ form the main layers consisting of hexagons, pentagons and triangles. Hexagons and pentagons of subsequent main layers form hexagonal and pentagonal antiprisms. The atoms between the main layers center the hexagons and pentagons and form secondary layers at approximately $z=\frac{1}{4}$ and $\frac{3}{4}$. Table 1 shows that the z parameters of all five secondary atoms deviate significantly from $\frac{1}{4}$, by as much as 0.0125 for 'atom' MnSi (26). This means that in the row of MnSi (26) 'atoms' the distances alternate between 2.444 and 2.211 Å.

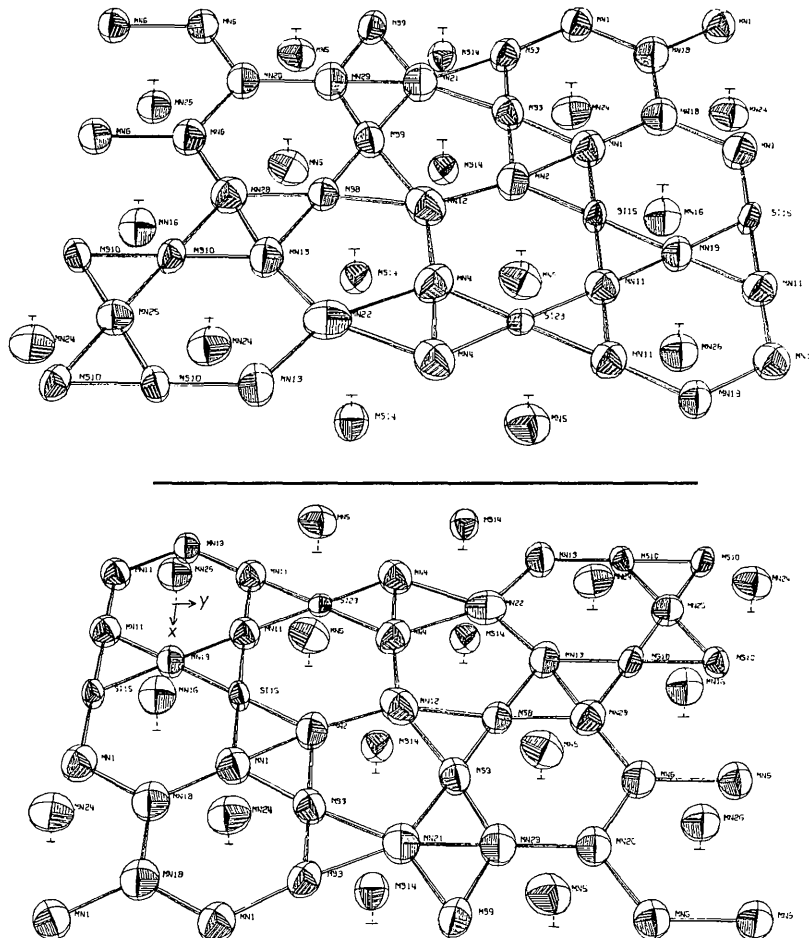


Fig. 1. The crystal structure of the ν phase, c axis vertical, looking 50° downward from horizontal. Thermal ellipsoids are drawn at 99.9999% probability; the ellipsoids of 50% are 0.258 as large in linear dimensions. Below: layer at $z=0$, atoms at $z \approx \frac{1}{4}$ on pedestals. Above: layer at $z=\frac{1}{2}$, atoms at $z \approx \frac{3}{4}$ suspended. Atoms in hexagons and pentagons at $z=\frac{1}{2}$ are staggered with respect to those below at $z=0$. MS stands for some mixture of Mn and Si; positions (24) and (26) should also have been labelled MS. This illustration was produced by the computer program *ORTEP* (Johnson, 1965).

The ν phase belongs to the family of σ -phase related, layered tetrahedrally close-packed structures, which are dense packings of atoms of different sizes, with only slightly irregular tetrahedral interstices and coordination numbers 12, 14, 15 and 16 (Shoemaker & Shoemaker, 1968). The percentages of atoms with CN 12, 14, 15 and 16 are respectively: 40, 43, 11 and 6, not far from those found in the P phase: 43, 36, 14, and 7 (Shoemaker, Shoemaker & Wilson, 1957). In α -Mn the percentages of atoms with CN 12, 13, and 16 are respectively: 41, 41, and 17. The relationship between the P and the ν phase is shown in Fig. 2. The ν phase may be derived from the P phase by replacing the local pseudo-mirrors in the P phase [parallel to the z axis and at an angle of about 16° with the y axis, indicated by horizontal bars in Fig. 2(b)] by real mirrors. On the main layers there are groups of four pentagons and four hexagons with intervening triangles present in the two structures in the same configuration. However, owing to the presence of the mirror planes, there are no parallel strips of pentagons and hexagons in the ν phase similar to those in the P phase. The secondary net of the ν phase cannot be generated by two sets of parallel zigzag lines, which makes classification difficult (Pearson & Shoemaker, 1969).

In Fig. 3 is shown how a main layer in the ν -phase structure may be described as having two different kinds of 'tiles' of pseudo-hexagonal symmetry each consisting of 7 hexagons and 12 triangles, one centered at $0, 0, 0$ and the other one at $\frac{1}{2}, \frac{1}{2}, 0$, with the space in between filled up by hexagons, pentagons and triangles. A 'tile' at $\frac{1}{2}, \frac{1}{2}, 0$ is surrounded in the same main layer by two tiles of the same kind (centered at $-\frac{1}{2}, \frac{1}{2}, 0$ and $+\frac{3}{2}, \frac{1}{2}, 0$) and four tiles of the other kind (centered at $0, 0, 0, \text{etc.}$). Above and below this tile are again tiles of the other kind. Frank & Kasper (1959) have described a hypothetical structure formed by tiles similar to the one occurring in this structure at $0, 0, 0$ of hexagonal symmetry and repeated in a hexagonal array. The interiors of the tiles in the ν phase contain atoms in the same arrangement as found in Zr_4Al_3 (Wilson, Thomas & Spooner, 1960). The latter structure contains perpendicular to the hexagonal z axis three layers of Zr atoms (two with CN 14 and one with CN 15) alternating with one layer of Al atoms (CN 12). As a result of the 'stepping' of the tiles in the ν phase atoms of different coordinations (and thus of different kinds) occur in the same layers.

Ordering of the atoms

The last column of Table 1 shows that all sites with CN 16 and 15, and all but two sites with CN 14, are occupied by Mn. Positions MnSi (24) and MnSi (26) contain about 10 and 30% Si respectively. The CN 12 sites are occupied by various mixtures of Mn and Si except positions Si(15) and Si(23), which contain only Si and positions Mn(11), Mn(19) and Mn(25) which contain only Mn. The average percentage Mn in the first coordination shell increases with the decrease of

the percentage Mn of the central site, and the two CN 12 sites that are occupied by Si have only Mn atoms in their first coordination shells. This may indicate some charge transfer from Mn to Si, since most of the Mn in the coordination shells are of 'type A' (coordination higher than 12).

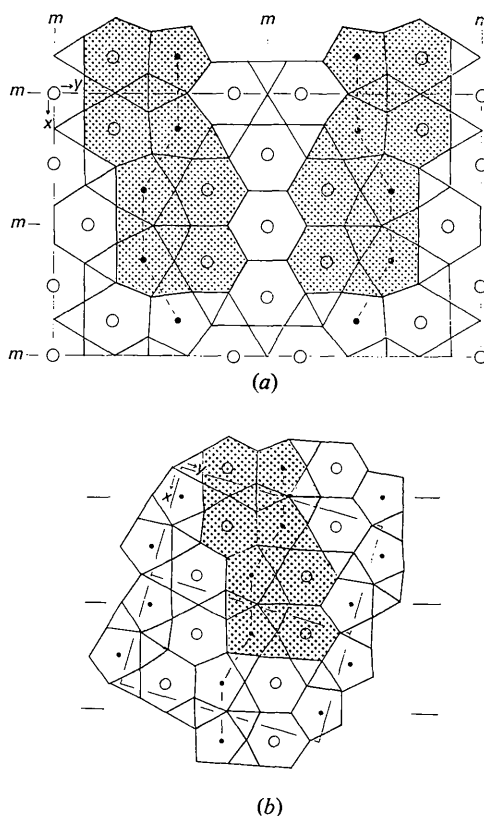


Fig. 2. Comparison of the structures of the ν phase and the P phase. Shaded areas indicate regions of similar arrangements. Circles indicate atoms between the mirror planes; closed circles: CN 12, open circles: CN 14. (a) Layer in mirror plane at $z=0$ in the ν phase, (b) layer in mirror plane at $z=\frac{1}{2}$ in the P phase. Horizontal lines give positions of vertical pseudo-mirror planes. Two P -phase unit-cells are lightly outlined with dashed lines.

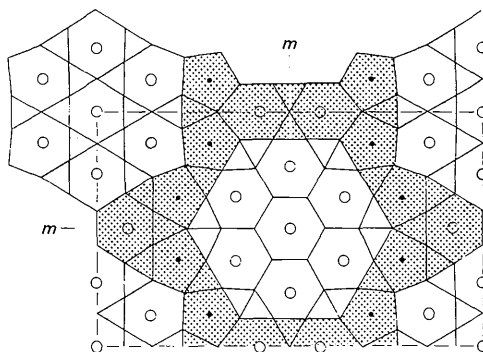


Fig. 3. Layer at $z=0$ in the ν phase. Non-shaded areas outline two types of 'tiles', each consisting of 7 hexagons and 12 triangles.

Table 3. Observed interatomic distances for the ν phase (\AA)

Standard deviations given by the least-squares procedure: 0.001—0.002 \AA . Reading down: underlined distances occur twice, those with wavy underlines four times. Asterisks indicate major bonds.

Atom	1 CN14	2 CN14	4 CN14	5 CN14	15 CN14	16 CN14	24 CN14	26 CN14	28 CN14	29 CN14	6 CN15	18 CN15	20 CN15	21 CN15
1		2.418*			<u>2.867</u>	<u>2.793</u>	<u>2.757</u>		<u>2.889</u>			<u>2.428*</u>		
2	2.418*			2.746	<u>2.943</u>				<u>2.857</u>					
4			2.387*	2.821						<u>2.869</u>				<u>2.924</u>
5		<u>2.746</u>	<u>2.821</u>	2.300*					<u>2.766</u>	<u>2.799</u>	<u>2.920</u>		<u>2.886</u>	
				2.356*										
13	<u>2.867</u>	<u>2.943</u>					<u>2.717</u>			2.421*				
16	<u>2.793</u>					2.295*			<u>2.801</u>		<u>2.899</u>	<u>2.944</u>		
						2.361*								
24	<u>2.757</u>						<u>2.717</u>		2.359*			<u>2.835</u>		
									2.297*					
26								2.444*			<u>2.804</u>		<u>2.852</u>	
								2.211*						
28	<u>2.889</u>	<u>2.857</u>		2.768	2.421*	<u>2.801</u>					2.465*			
29			<u>2.869</u>	2.799									2.491*	2.527*
6				2.920		<u>2.899</u>		<u>2.804</u>	2.465*		2.590*		<u>2.597*</u>	
18	2.428*					2.944	<u>2.825</u>					2.490*		
20				2.888				<u>2.852</u>		2.494*	2.597*			
21			<u>2.924</u>							2.527*				
12		2.536*	2.644*	3.196										
22			2.937		2.600*		3.279							<u>2.683*</u>
3	2.515	2.577			<u>2.532</u>		<u>2.537</u>							<u>2.717</u>
8		<u>2.544</u>		2.562	2.601				2.523					
9			<u>2.558</u>	2.547						<u>2.519</u>				<u>2.652</u>
10	<u>2.529</u>				2.463	<u>2.549</u>	<u>2.565</u>		2.510			<u>2.737</u>		
11				2.559				<u>2.616</u>			<u>2.664</u>		<u>2.668</u>	<u>2.652</u>
14		<u>2.620</u>	<u>2.577</u>		<u>2.597</u>				<u>2.519</u>		<u>2.770</u>			
15	2.466	2.442		2.590		<u>2.569</u>					<u>2.664</u>			
19						2.551		<u>2.598</u>						
23			2.473	2.571						<u>2.529</u>				<u>2.772</u>
25							2.561					<u>2.640</u>		
Atom	12 CN16	22 CN16	3 CN12	8 CN12	9 CN12	10 CN12	11 CN12	14 CN12	15 CN12	19 CN12	23 CN12	25 CN12		
1			2.515			<u>2.530</u>			2.466					
2	2.536*		2.577	<u>2.544</u>				2.620	2.442					
4	2.644*	<u>2.937</u>			<u>2.558</u>			2.577			<u>2.473</u>			
5	<u>2.196</u>				<u>2.562</u>	<u>2.547</u>		<u>2.229</u>	<u>2.290</u>		<u>2.571</u>			
13		<u>2.600*</u>	<u>2.532</u>		2.601		2.463	2.597						
16						<u>2.549</u>			<u>2.569</u>	<u>2.551</u>				
24		<u>2.279</u>	<u>2.537</u>			<u>2.565</u>						<u>2.561</u>		
26							<u>2.616</u>		<u>2.598</u>					
28				2.523		2.510			<u>2.519</u>					
29					2.519						<u>2.529</u>			
6							<u>2.664</u>		<u>2.770</u>	<u>2.664</u>		<u>2.640</u>		
18						<u>2.737</u>								
20							<u>2.667</u>				<u>2.772</u>			
21		<u>2.683*</u>	2.717		2.652			2.654						
12	<u>2.789*</u>			2.758	2.870			2.709						
22			<u>2.834</u>	<u>2.779</u>	<u>2.854</u>			2.651						
								2.641						
3		<u>2.834</u>	2.330					2.402						
8	2.758				2.358			2.422						
9	<u>2.772</u>							2.386						
	2.870			2.358										
	<u>2.824</u>													
10						2.430				2.385	2.314	2.415		
11							2.292					<u>2.352</u>		
14	<u>2.709</u>	<u>2.641</u>	<u>2.402</u>	<u>2.422</u>	<u>2.386</u>			2.342	2.313					
	<u>2.651</u>													
15								2.385			<u>2.387</u>			
19								2.514		2.387				
23								2.415						
25						2.355								

Interatomic distances

The interatomic distances are given in Table 3. The range is 2.211–3.279 Å (next largest: 3.196 Å), as compared with 2.24–2.96 Å in α -Mn. As in other tetrahedrally close-packed structures, we have analyzed the distances in terms of sums of radii of atoms of certain coordination type (Shoemaker & Shoemaker, 1964). The 111 crystallographically independent distances were expressed as the sums of 42 different radii: one radius (r) for each CN 12 atom and two radii [one (r) for 5-coordinated, minor, bonds and one (r^*) for 6-coordinated, major, bonds] for each CN 14, 15 and 16 atom. The values for these radii that give the best least-squares fit to the observed distances are given in Table 4, together with the average value for each type of radius and the predicted values (in parentheses) derived from the average weighted CN 12 radius (Shoemaker & Shoemaker, 1964). In the calculation of the average radius the CN 12 radii 1.268 and 1.260 were used for Mn and Si respectively. The agreement between the observed average radii and the predicted values is rather good (largest deviation: 0.07 Å), although less good than for some other tetrahedrally close-packed structures (e.g. the M phase, Shoemaker & Shoemaker, 1967). In general the deviation from the predicted values for this kind of structure is upward for r_{14}^* , upward for r_{16} and downward for r_{16}^* . The radii are largely determined by the CN of the site, rather than by the occupancy. In the case of the CN 12 radii, there is no correlation between the observed radii of the sites and the occupancy by Mn, Si or a mixture of the two. In the case of CN 14 the positions MnSi(24) and MnSi(26), which have some Si admixed in them have the smallest observed radii for CN 14, but it is doubtful whether this is a meaningful correlation. The largest deviation between the distances calculated on the basis of the averaged observed radii and the observed distances is 0.256 Å (next largest 0.174) and the mean deviation is 0.047 Å.

Table 4. Summary of atomic radii for the ν phase

CN	Atom	r	r^*
14	Mn(1)	1.400	1.231
	Mn(2)	1.417	1.163
	Mn(4)	1.403	1.211
	Mn(5)	1.404	1.164
	Mn(13)	1.416	1.251
	Mn(16)	1.396	1.164
	MnSi(24)	1.378	1.164
	MnSi(26)	1.374	1.164
	Mn(28)	1.400	1.170
	Mn(29)	1.403	1.192
		$\overline{1.401}$ (1.40)	$\overline{1.186}$ (1.14)
15	Mn(6)	1.504	1.294
	Mn(18)	1.513	1.221
	Mn(20)	1.504	1.302
	Mn(21)	1.515	1.335
		$\overline{1.508}$ (1.47)	$\overline{1.289}$ (1.28)
16	Mn(12)	1.623	1.397
	Mn(22)	1.620	1.348
		$\overline{1.622}$ (1.55)	$\overline{1.373}$ (1.41)

Table 4 (cont.)

12	MnSi(3)	1.175
	MnSi(8)	1.170
	MnSi(9)	1.179
	MnSi(10)	1.167
	Mn(11)	1.180
	MnSi(14)	1.155
	Si(15)	1.166
	Mn(19)	1.176
	Si(23)	1.172
	Mn(25)	1.166
	$\overline{1.169}$ (1.15)	

The 6-coordinated or major bonds form two non-interconnected three-dimensional nets with additional rows of CN 14 atoms as in the P phase. The angles between the major bonds vary between 168.3 and 180.0° for the CN 14 atoms (ideally 180°), between 117.8 and 121.1 for the CN 15 atoms (ideally 120°), and between 100.9 and 113.2 for the CN 16 atoms (ideally 109.5°).

Thermal parameters

Because of the possibility that the B_{ii} might be highly correlated with the occupancy factors, these parameters were not refined together until the final cycles. At the end of the refinement, the correlation coefficients between the B_{ii} 's and the occupancy factor of an atom were found to be in the range 0.40–0.52. All atoms have twelve minor bonds and in addition the CN 14 atoms have two major bonds along a straight line, the CN 15 atoms have three major bonds in a plane and the CN 16 atoms have four major bonds, tetrahedrally directed. One might therefore expect approximately isotropic temperature factors for

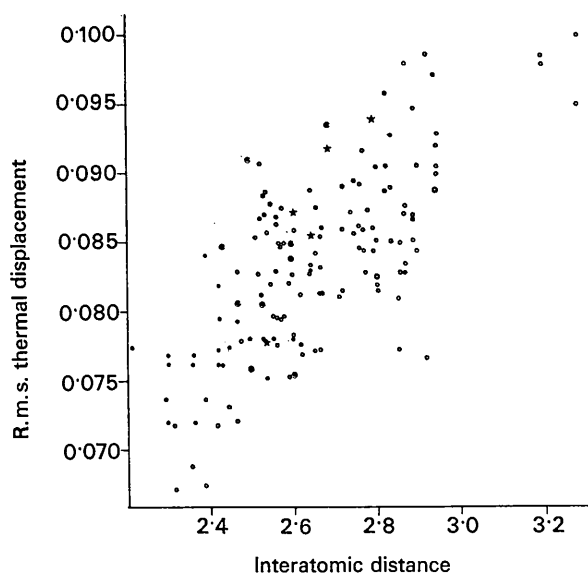


Fig. 4. Root-mean-square vibrational displacement (Å) in the direction of a bond for the Mn atoms plotted against the length of that bond (Å). Stars indicate major bonds of CN 16 atoms, circled dots indicate major bonds of CN 15 atoms, black dots indicate major bonds of CN 14 atoms, open circles indicate minor bonds of all types of coordination.

CN 12 and CN 16 atoms and anisotropic temperature factors for CN 14 and CN 15 atoms with the smallest displacement for CN 14 atoms along a major bond and the largest displacement for CN 15 atoms perpendicular to the plane formed by the major bonds. The results for some atoms are in agreement with this, but on the whole there is a better correlation between the root-mean-square displacement in the direction of a bond and the observed interatomic distance. Of the CN 14 atoms, atoms 1, 2, 28, 29 and the in-between atoms 5, 16, 24, 26 have thermal ellipsoids with one short axis and two other axes of approximately the same length, with the short axis more or less lined up in the direction of a major bond, although in some cases the deviation from isotropy is not significant. For atoms 4 and 13 the short axis is not lined up along a major bond. For all the CN 15 atoms the ellipsoid axis of intermediate length is perpendicular to the plane of the major bonds, but in most cases there is no significant difference between the two larger axes. The thermal motion of the two CN 16 atoms is significantly anisotropic with an increase in thermal displacement with the length of the interatomic distance. In the case of the CN 12 atoms a further complication arises from the difference in occupancy. Atoms 15 and 23, which are occupied by Si alone have significantly smaller thermal ellipsoids than the other atoms. This may be a result of an inadequate scattering factor curve used for Si. Alternatively, if about 10% Mn were present in these positions, the thermal parameters would increase to about the average values. An increase of scattering power at the Si sites by transfer of some electrons to these sites would also result in higher temperature factors. This structure determination is not accurate enough to draw firm conclusions in this regard. The CN 12 positions occupied by mixtures have mostly anisotropic temperature factors, but there is no good correlation between the displacements and the interatomic distances. On the other hand the CN 12 positions occupied by 100% Mn (11, 19, 25) have a rather good correlation between thermal displacement and interatomic distance.

Fig. 4 shows the root-mean-square vibrational displacement in the direction of a bond plotted against the length of that bond. Of the CN 12 positions only those occupied by Mn without appreciable content of Si are plotted. The standard deviations in the displacements, calculated from the standard deviations in the thermal parameters, are about 0.003. Although there is a large spread there seems to be a definite correlation between

the length of an interatomic distance and the r.m.s. vibrational displacement in that direction.

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