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 3,4dimethyl 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 v Phase, Mn_{81.5} Si_{18.5}*

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The crystal structure of the v phase, Mn₈₁·5Si₁₈·5 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 *Immn* (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 v 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 v 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 v 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 fourcircle General Electric diffractometer with Mo $K\alpha$ radiation. A θ -2 θ scan was used and 3373 independent reflections were recorded out to 2θ =75°. 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:

$$a_0 = 16.992$$
 (4), $b_0 = 28.634$ (7), $c_0 = 4.6556$ (14) Å.

There were no systematic extinctions other than those for body-centering. Possible space groups are: I222 (D_2^8) , $I2_12_12_1$ (D_2^9) , 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 $\mu=215$ 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 v phase shows a concentration of high intensities in shells in reciprocal space at about 1/d = 0.48, 0.90 and 1.44 Å⁻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 v 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 leastsquares 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 $l \le 2$ 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 Rto 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 $l \le 2$ 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 $F_{a}^{corr} =$ $F_{a}(1+gI_{a})$ with $g=1.33\times10^{-5}$ (Zachariasen, 1963).

		%Mn	100.0	0.001	0.001	0.001	0.001	0.001	C-06	69.4	0.001	0.001	100.0	0.001	0.001	0.001	100.0	0-001	59-1	49.1	50.2	30.7	100.0	75.0	0.0	0.001	0.001	0-001
		f_0	25·5 (2)	25·5 (2)		(1) 9.07	(7) 5.07	$(7) \\ (7) $	$24 \cdot 3$ (2)	$(7) 6 \cdot 17$	25-3 (2)	(7) 8.07	24·9 (2)	25.9 (2)	25.0 (2)	(7) C-C7	25-0 (2)	25-0 (2)	20.8 (2)	19.6 (2)	19.8 (2)	17.5 (2)	25-3 (2)	22·5 (1)	13-6 (2)	(7) 7.07	13.0 (2)	(7) 7.07
	$(k+\cdots)$].	B_{23}				-0-12 (2)			0.05 (3)															-0.01 (2)				
	$+2a_1*a_2*B_{12}h$	B_{13}				-0.01 (2)		-0.08 (2)																0.03 (2)				
	$*^2B_{11}h^2+\cdots$	B_{12}	0.04 (2)	-0.03 (2)	-0.09 (2)	0.03 (2)	-0.03 (2)				-0.04 (2)		-0.02 (2)				0.18 (2)		0-09 (3)	-0.01(3)	0-08 (3)	-0.08 (3)	0.03(2)	0.00 (2)	0.03 (4)			
4	n: exp [- 1 /a	B_{33}	0.66 (4)	0-65 (4)	0.60(3)	0.48 (2)	0-64 (4)	0-42 (3)	0-47 (4)	0-47 (6)	0.61 (4)	0-62 (5)	0-58 (4)	0.61 (5)	0.59 (5)	0-78 (5)	0-66 (4)	0.63 (5)	0-58 (4)	0.52(5)	0.55(5)	0.54(5)	0.57(3)	0.41(3)	0.67 (7)	0.54 (5)	0.31(9)	0-66 (7)
\$	or expression	B_{22}	0.48 (3)	0-41 (3)	0.56 (3)	0·72 (2)	0-41 (3)	0.56 (3)	0.71(3)	0-53 (5)	0-52 (3)	0-48 (4)	0.45 (3)	0.54 (4)	0-45 (5)	0-51 (5)	0.63 (3)	0.82 (5)	0.42 (4)	0.37 (4)	0.39(4)	0.28(4)	0.43 (3)	0.40 (2)	0.19 (6)	0.33 (4)	0.26 (9)	0-47 (6)
7	rature fact	B_{11}	0-54 (3)	0.57(3)	0.57 (3)	0.66 (2)	0.63 (3)	0.66(3)	0.61(3)	0.56 (5)	0.54 (3)	0-71 (4)	0-57 (3)	0.65 (4)	0.62 (4)	0-58 (4)	0.60 (3)	0-51 (4)	0.50 (4)	0.47 (4)	0.60(4)	0.42 (4)	0.43 (3)	0-49 (2)	0.23 (6)	0-47 (4)	0·23 (8)	0-35 (6)
	se for the tempe	14	0	0	0	0.24703 (16)	0	0.24648 (22)	0.25332 (24)	0.26250(37)	0	0	0	0	0	0	0	0	c	~ c	• C	• C	- C	0.25156 (17)	0	0	0	0
) listed are thos	2	0-07262 (3)	0.14505 (3)	0.22005 (4)	0.36105 (2)	0.37155(3)	*	0.42061 (4)	0	0-41106 (3)	0-32107 (5)	0-45478 (4)		0.40817 (5)	0.23281(5)	0-22751 (4)	0-31376 (5)	0.14709 (4)	0.22206 (1)	0.222/0 (1)	0.45757 (5)	(2) 10104 0	0.20909 (3)	0.07125 (7)	0	0.14441 (9)	4
	he <i>B</i> values (Å ²	x	0 35291 (5)	0.27979(5)	0.07025 (5)	0.36581 (4)	0.11799 (6)	0.23201 (5)	0		0.24397 (6)	2 2	0.36897 (6)	0.42673 (8)	(0) (107+0) *	7-10	0.22534 (6)	0	(7) 2113 (7)		(1) CC147.0	(1) 110100	0.06744 (5)	(c) 44 (c)	0-20780 (10)	0.13492 (8)	0	0
	T	Site	8(n)	8(n)	8(n)	16(n)	8(n)	(iii)0	8(1)	4(i) 4(i)	8(n)	4(h)	(u)8	(II)0 1(A)	4(h)	4(h)	(1)8	4(g) 4(g)	(-)0		(11)0	(11)0	0(II) 0(1)	(II)0 16(A)	8(n)	() (e)	4(g)	2(d)
		Atom	Mp(1)	Mn(2)	$M_{n}(4)$	Mn(5)	Mn(13)	(CI)/IM	M nSi(24)	MnSi(76)	Mn(28)	Mn(29)	Mn(6)	Ma(18)	Mn(20)	Mn(21)	(CI)-M	Mn(22)				(6)ICHIM	MIDSI(10)	Min(11) MinSi(14)	Si(15)	Mn(19)	Si(23)	Mn(25)
		Z	5 2	1 1	14	14		t -	<u>_</u> t	<u>+</u> -	1 1	14	15	24	2 4	15	21	16		7	19	19	22	12	12	12	15	12

Table 1. Atomic parameters for the v phase

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 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 in are given Table 2. The values entered in the F_0

Table 2. Observed (left column) and calculated (right column) structure factors for the v 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 now; for subsequent reflections k steps by +2.

HCL 0 2 0 40 -76 271 277 139 -142 17* -23 65 65	65 -66 65 -69 96 95 59 -59 181 189	344 18 234 -5 178 -175, 40 48	43 -40 144 138 274 0 58 58 304 8
4* 31 76 -47 79 40 137 -147 19* 9 51 41	159 29 65 -60 62 -34 299 -19 229 -12 H	41 24 0 2 244 -12 180 -176 120 120	285 282 92 -75 HKL 21 1 4 234 -17 135 -108
11* -1 135 129 27* 17 279 -291 137 100 21* 41	182 -186 61 -64 134 139 138 137 289 290	144 144 100 103 378 38 258 -5	744 700 321 14 354 -14 51 337
45 34 238-246 49 46 147 145 147-192 288 41	304 330 150 152 59 53 76 -64 84 80 140 192 67 71 71 65 214 32 234 8 174 -13 51 -57 HKL 31 2 110 108 344 -49 132 -138 41 -41 245 22 91 95 78 -73	225 - 220 224 33 270 - 0 150 -10	210 -243 38* -41 70 -69 81 72 107 110
78 75 208-15 85 -74 423 436 102 101 288-25		90 - 00 230 27 HKL 13 0 3 78 - 73	40 44 134 -133 25* -23 22* 22 31* -12
86 64 98 -101 348 -15 261 -266 216 212 338 38		40 21 440 47 104 -100 287 290	25* 27 HKL 12 0 4 416 423 164 -38 93 -92
U 123 70 74 MEL 13 10 115 124 48 40 346 358		70 74 380 38 137 - 143 76 75	75 -77 22* -16 36* -36 28* -9 46 -42
1422 1467 18* -3 18* -18* 175 -17* 211 -20* 155 155	50 -50 105 -111 371 -348 134 -7 237 235	77 -79 HKL 6 1 3 206 214 378 -46	204 217 61 69 177 -172 44 -21 378 -28
34* 42 19* 2 13* -17* 77 -7* 75 10* 11	294 -35 344 31 981 -920 92 -49 244 -2	242 -239 100 -95 103 -108 248 10	204 -223 37 27 138 -140 89 80 264 -3
14* -31 20* 4 18* 6 80 -32 53 57 25* -22	214 -7 112 -112 242 239 234 22 135 -137	76 75 89 AT 110 -112 278 22	242 256 52 -53 264 -6 MRL 6 1 5 180 179
	255 245 95 105 492 -502 102 108 78 -79	248 -40 231 -235 140 147 HKL 22 1 3	141 -147 113 -128 52 -53 74 -66 89 87
901 865 73 -77 97 66 23 8 12* 10 174 -177 258 266 -7 -55 314 -351 92 -85 100 27* -5 258 210 222 237 26% -302 28* -24 156 166 #4CL 8.1 724 777 123 -127 210* -22 41* -24 156 166 #4CL 8.1 734 777 123 -127 210* -22 41* -24 19* -203 781 -731	145 146 180 31 70 -72 240 7 HHL 17 1 2 210 26 68 73 86 90 153 147 43 40 4 47 -40 168 -163 117 117 -370 31 54 53 65 70 230 -18 321 -322 240 18 87 -92	123 -118 16* 12 20* -5 51 -68 KL 27 L 2 103 -93 20* 3 43 -34 80 -76 139 130 96 -103 24* -28 103 -96 147 -127 153 151 14* 14*	+2 -+5 272 285 50 58 62 58 HEL 15 0 122 123 570 591 256 248 180 -174 119 -116 357 351 153 -158 164 61 13* -11 37* 36 126 124 63 62 HKL 22 0 47 -79 21* -13
1/2 30 25 26 10 10 10 10 10 31 35 270 272	179 -178 279 6 630 -619 HKL 10 0 2 136 -144	171 -168 84 -75 91 -80 79 75	50 -52 28* 25 252 252 93 97 48 28
6.4 55 26 - 1 7- 74 HKL 21 10 20 17 62 -62	339 38 HKL 23 0 1 269 -22 32 24 45 -49	56 -52 169 -6 229 -1 99 -53	128 125 104 -113 81 -83 90 -85 45 -39
12 13 17 -180 187 -190 31 -20 24 -15 260 244	183 176 205 -208 68 -57 284 -289 111 115	278 -18 150 -148 74 -78 399 -51 H	KL 5 1 4 87 94 121 120 61 -63 21* 29
42 -50 11 - 11 10 22 -91 27 -41 135 129	HKL 15 0 1 50 46 223 -222 43 -40 229 236	57 51 55 -46 238 -7 85 -80	72 -74 77 -73 101 99 24* -13 24* -10
200 23 HCL 71 0 103 -107 314 -24 234 14 129 -16 200 215 228 219 107 -101 533 557 339 30 48 54 337 350 148 3 129 -112 378 -46 348 35 49 -24 314 325 -490 39 154 167 223 -225 HKL 2 1 1 39 27	137 -156 38 20 45 -37 306 309 45 50 95 92 154 155 128 19 270 270 55 -51 H 259 -24 93 90 131 -125 81 -75 103 -105 62 66 52 66 245 -245 356 -336 55 -53	30* 25 20* 15 30* -30 33* 32 KL 28 0 2 147 146 74 -68 97 -90 255 247 262 264 63 73 112 104 30* -21 58 50 87 -74 43 39	164 -10 153 169 113 117 113 -118 88 90 114 12 52 -53 103 95 47 -47 125 129 16* 12 71 -55 446 -31 23* 3 25* -16 31 32 158 160 181 171 103 115 47 -41
124 118 154 1533 84 -81 180 -182 39 40 33 18	39 -37 75 14% -6 32 -29 49 -55 52 53 35# 40 72 -70 60 64 139 164 139 164 139 164 139 164 139 164 139 164 171 24% -16 25% 16 197 193 28% -19	179 -6 65 -63 156 149 67 65	16* 5 217 210 39 -20 189 -193 183 -179
158 152 40 -77 159 160 239 -7 37 41 58 -49		KL 0 1 3 309 -34 46 -24 MKL 23 0 3	170 -185 63 69 27* -2 32* 25 23* -36
MAL 1 13 24* 14 149 -118 70 -71 71 -63 500 -535		45 67 219 17 MKL 14 1 3 171 -164	63 -59 HKL 13 1 4 155 149 64 -61 27* 11
40 -4 8* -2 70 -77 76 718 118 -109 139 134		35 34 319 -26 360 373 57 55	21* 23 120 -130 HKL 23 1 4 37* -33 108 102
30 26 30 -26 317 318 10* 27 14 13 66 70 32 -17 151 -150 100 -100 50 36 41 33 66 70 41 31 331 347 HL 14 0 95 -44 100 96 23* 24 108 -2.6 96.0 96.2 1100 112* 95 -44 100 96 23* 24*	222 230 46 80 144 147 88 86 99 101 259 -26 109 112 268 19 122 122 66 60 56 -56 330 -34 216 -206 173 -173 248 30 237 -242 113 109 MRL 6 0 2 199 -11 MRL 18 0 2	36 58 43* 41 118 -127 25* 23 19* 18 141 -133 65 -69 147 146 19* 18 141 -133 65 -69 147 146 19* 18 34* -13 66 -36 96 96 275 -282 HKL 7 0.3 28* 37 56 45	62 75 90 -96 156 152 17* 8 HKL 16 1 5 93 -96 21* 3 33* 33 HKL 7 0 5 184 -193 21* 12 94 -100 44 -41 267 -252 90 101 24* 41 64 63 205 208 63 66 24# -4
100 -100 210 214 88 -11 20 17 30 -36 215 225	43 -38 34 32 247 268 121 120 221 227	853 872 304 -301 154 -156 71 79	164 -170 244 -249 250 -13 173 -167 41 45 250 23 206 -214 270 -1 490 455 55 54 64 67 159 -161 244 33 301 297 250 -29 102 97 45 48 274 -7 330 -33 103 100
30 75 231 -230 114 14 30 -23 70 67 54 98	328 29 MHL 24 1 1 825 -946 226 -24 352 -376	374 388 152 155 430 444 51 50	
134 -130 64 30 -16 -40 51 31 86 -78 80 80	172 168 231 -256 430 -458 94 69 172 -175	118 17 240 -249 171 176 144 143	
109 109 101 40 110 -6 44 12 00 100 105 102 -14	108 97 102 103 134 128 61 -67 105 112	47 49 724 744 13# -0 268 -12	
39 56 228 227 73 76 111 -112 89 -92 778 -245 149 149 441 459 869 879 157 157 100 22 6 MKL 9 01 492 -635 115 119 149 -16 125 100 22 6 MKL 9 01 107 99 779 -700 178 -2 147 145 74 97 139 135	131 -126 123 127 134 -2 153 -159 218 -21 404 42 60 53 42 -45 368 28 358 -367 339 34 314 -29 39 -35 58 44 103 104 178 -1 429 -45 364 -144 97 11 3 4 -85	505 -550 32 -37 24* -31 85 -81 43 -36 15* 5 14* -17 HKL 24 1 3 455 476 19* -11 23* -3 224 -224	118 -165 145 -145 HXL 24 0 4 44 -27 254 0 128 -105 145 -145 HXL 24 0 4 44 -27 254 0 137 102 85 83 152 158 114 116 77 81 79 -77 157 -151 388 0 149 -153 109 -101
27************************************	HEL 16 1 200 13 430 -022 44 66 174 -135 286 -299 43 -29 260 3 373 -378 46 43 138 162 74 67 110 114 861 -451 59 50	112 117 230 -216 147 140 28* -16 135 -141 565 549 25* 32 122 120 191 202 81 85 36* -30 57 54	304 -23 86 -66 34# 20 216 19 38# 31 189 -4 135 127 80 -73 24# 14 30# 18 40 -33 62 -64 45# 47 24# 14 30# 18
27# 28 mc 305 325 24.8 0 8.9 -4.8 27# -2.6 278 288 1.08 1.08 1.08 1.08 1.08 2.7 2.00 1.07 1.08 1.08 2.0 2.7 2.27 2.28 6.3 6.2 2.20 1.90 <t< td=""><td>99 96 156 -153 512 -522 549 -545 177 -149 106 106 67 .55 200 -23 42 -36 320 -6 52 -48 113 -109 49 -36 200 26 58 61 135 136 WI 25 01 237 -238 41 43 127 -127</td><td>62 59 138 26 152 -149 54 -42 246 241 59 51 HKL 15 0 3 208 14 126 122 288 -1 98 -100 48 -24</td><td>125 -126 HKL 16 0 4 HKL 25 1 4 238 -26 259 38 46 41 737 754 131 -127 338 23 228 -20 35 -29 62 -64 51 -37 252 241 56 -47</td></t<>	99 96 156 -153 512 -522 549 -545 177 -149 106 106 67 .55 200 -23 42 -36 320 -6 52 -48 113 -109 49 -36 200 26 58 61 135 136 WI 25 01 237 -238 41 43 127 -127	62 59 138 26 152 -149 54 -42 246 241 59 51 HKL 15 0 3 208 14 126 122 288 -1 98 -100 48 -24	125 -126 HKL 16 0 4 HKL 25 1 4 238 -26 259 38 46 41 737 754 131 -127 338 23 228 -20 35 -29 62 -64 51 -37 252 241 56 -47
200 265 162 156 62 60 258 25 256 256 158 −18	112 108 147 154 430 440 423 426 410 57 1	KL 1 0 3 312 306 20* -18 MKL 25 0 3	78 78 78 219 27 HKL 0 15 HKL 8 15 329 -15
209 −212 606 52 606 35 111 100 67 66 92 69	200 3 300 41 48 -65 564 -578 124 -110	30 30 153 157 64 68 142 139	157 -170 23* 5 28* -11 372 -406 63 -40
179 −50 252 266 119 116 66 50 99 −5 120 119	130 137 158 -165 157 -161 170 26 MKL 10 1 2	43 39 112 118 20* -5 29* 40	139 -11 22* -18 21* 15 143 13* 62 65
NGL 2 0 0 103 −102 312 316 136 −123 109 −5 136 139	129 -132 58 88 322 -130 157 -159 210 -1	26 24 24* -13 48 50 135 -136	73 -73 -73 44 50 18* 27 64 -54 45 55
10* 35 1*4 1*2 HL 15 10 HL 23 10 324 -300 65 -47	300 -304 27* -19 37 -92 285 -290 144 -145	148 -6 249 8 329 24 56 49	44 52 613 651 35 -40 124 113 164 -24
9* 22 53 57 3*4 371 198 198 151 -135 105 109	51 47 100 -88 122 127 92 -89 456 -480	279 26 HKL 8 1 3 170 169 249 -20	204 -5 254 -12 79 76 344 49 348 32
37 37 175 -172 89 91 42 42 151 -137 65 61	-234 22 86 -90 313 -311 200 -16 163 169	72 74 513 -543 216 218 74 -72	238 1 238 -8 143 -189 244 -6 49 45
9* -90 86 81 101 -99 60 -53 227 216 33* -51	85. 83 50 35 MKL 9 1 2 218 -210 264 -271	119 -121 231 209 318 -21	219 0 44 17 554 72 37 26 44 -6 49 45
168 -149 712 720 235 246 255 240 48 -35 210 4	67 73 240 -6 247 251 210 -201 106 109	103 100 32 -22 41 -44 428 36	155 -150 75 89 213 217 40 -32 224 -15
60 63 465 491 53 -53 240 -17 39 -40 86 86	276 -5 136 -133 42 -42 240 32 30 36	164 184 225 227 163 -162 274 -5	64 -59 108 -108 210 -7 294 6 116 -125
44 44 133 -130 32 -29 240 0 52 50 73 73	61 62 48 40 455 -442 79 -81 140 -32	316 27 138 130 334 -22 MRL 26 1 3	45 -37 170 170 140 8 206 -1 254 -1
70 -15 105 107 147 159 400 39 177 -172 82 -73	95 99 49 30 266 267 247 -242 180 -181	152 -163 179 -12 306 36 276 -9	195 182 199 402 132 -130 46 -48 8 1 -81
110 103 20* 5 136 144 24* -8 85 -*3 34* 35	298 -11 56 66 136 -124 338 -5 358 -368	37 -39 58 60 141 161 27# -18	102 -131 23* 15 417 -440 326 -332 25* -10
61 -40 151 -157 ** 9 *7* 46 *4 36 27* 5	HKL 17 0 1 HKL 26 1 1 44 36 172 -171 45 57	55 56 38 13 110 102 65 42 H	KL 7 1 4 85 -72 26* -31 96 84 183 -177
82 -67 176 185 22* 31 38* 10 231 23* #4(10 1	261 267 254 -13 98 91 HKL 12 0 2 80 -79	22# 21 45 31 93 42 118 -113	132 128 27* 0 334 352 108 -95 101 97
80 -*5 23* -32 1*6 202 263 25* 180 -134 140 -13	63 67 47 -99 82 78 225 236 151 -151	324 28 304 32 110 -111 344 37	188 0 HKL 15 1 4 140 143 14* 24 133 -132
159 -6 229 234 298 296 225 214 48 -47 82 -82	10 -45 51 50 160 -17 410 -421 114 -100	112 103 289 -18 54 58 82 -83	18* 21 254 263 46 63 26* 8 87 -88
155 113 98 -88 231 -229 444 -44 191 -197 26 -21	70 -72 135 -137 360 -347 156 -151 370 -31	130 143 408 -400 KKL 16 1 3 KKL 0 0 4	932 935 70 64 119 -122 112 -100 27* -18
239 20 54 33 173 174 348 36 74 46 45 -39	45 -44 400 36 82 79 130 129 80 -61	170 -177 123 115 226 -238 1883 2000	47 -47 65 -69 131 137 148 142 38* 25
70 -71 225 22 137 135 278 19 40 -47 98 -	200 -17 114 -108 115 112 T0 -67 117 -116	378 47 125 -126 130 137 308 15	19* 3 171 183 5* -62 H4t 9 0 5 42* -40
63 64 62° 40 138 140 ×41 24 0 0 24° -8 121-124	80 -85 112 109 58 53 204 206 115 103 94 101 117 -113 19* -23 114 112 HKL 20 2 85 85 344 -15 22 21 21* 25 42 -44 35 -37 27* 27 44 52 96 -93 49 -47	154 27 92 87 36 27 176 -1	46 43 36 -36 HKL 1 0 5 71 61 HKL 10 0 5
108-110 ×41 91 0 390-28 199 206 107 146 14°		238 -6 51 40 97 98 248 24	102 -95 32* -24 25* -17 58 59 45 -38
310 -33 230 -228 25° 32 15° 2 62 -43 257 -248		61 -32 109 -112 102 105 188 37	228 230 120 117 25* -4 13* -11 32* 33
120 125 28 20 73 74 79 -73 38° -37 113'-110		178 19 202 204 46 -42 52 49	857 869 109 105 12* 23 67 48 32* 17
210 -16 2/* 16 247 -242 24 27 445 -40 228 14	132 -139 170 -26 140 -144 156 -156 104 -107	<pre>%L 2 1 3 106 101 140 139 64 85</pre>	169 193 72 71 20* -17 85 7 78 71 61
224 28 48 35 252 250 91 -81 Hott, 41 1 100 55	41 52 KGL 27 0 1 48 53 120 14 51 52	299 24 91 84 109 110 865 900	161 -167 24* 22 18* -3 28* 14 28* -19
102 -106 65 -78 Hott, 16 0.0 68 61 77 -76 117 25	84 76 440 -47 44 -44 75 73 129 -115	30 32 134 -126 229 9 129 22	47 46 161 160 37 42 24* -23 85 -79
246 3 180 -13 874 -053 259 0 54 -73 75 -68	55 60 91 -89 73 79 195 -201 173 176	36 -30 389 33 133 130 179 -22	76 77 228 224 100 -107 14* 1 135 -135
mtl 1 0 20 ⁻¹⁰⁷ 45 ⁻¹⁰ 120 ⁻¹⁰⁵ 20 86 73 ⁻¹⁰ 200 23 23 23 120 ⁻¹⁰⁷ 120 ⁻¹⁰⁵ 100 ⁻¹⁰⁷ 200 23 23 23 23 120 ⁻¹⁰⁷ 100 ⁻¹⁰⁷ 26 -43 26 ⁻¹⁰⁷ 26 ⁻¹⁰⁷ 26 ⁻¹⁰⁷ 120 ⁻¹⁰⁷ 120 ⁻¹⁰⁷ 26 -43 26 ⁻¹⁰⁷ 26 ⁻¹⁰⁷ 120 ⁻¹⁰⁷ 120 ⁻¹⁰⁷ 120 ⁻¹⁰⁶ 26 -43 87 70 ⁻¹⁰⁶ 100 ⁻¹⁰⁷ 120 ⁻¹⁰⁷ 120 ⁻¹⁰⁶ 26 -43 87 70 ⁻¹⁰⁶ 100 ⁻¹⁰⁶ 100 ⁻¹⁰⁶ 100 ⁻¹⁰⁶ 26 -40 80 80 ⁻¹⁰⁶ 100 ⁻¹⁰⁶ 100 ⁻¹⁰⁶ 100 ⁻¹⁰⁶	270 33 139 130 340 52 323 533 180 180 1 270 31 280 -14 90 -86 68 84 168 -153 55 50 240 -3 380 39 236 0 127 121 161 -155 360 -36 861 6 0 2 260 -16 131 -127 44 -35 340 -36 841 -60 2 260 -16 131 -127	13* 25 118 121 248 -251 554 605 27 25 110 114 41 41 186 191 65 60 21* -20 49 20 139 145	71 -73 173 -175 350 37 100 107 200 0 175 179 134 133 103 100 230 -20 50 36 354 352 104 105 38 24 230 -5 270 12 92 91 124 111 111 -117 340 50 52 52
154 -147 107 -107 37 -32 156 145 122 -113 11 -45 314 -23 154 -141 155 59 -9 -76 78 -77 83 -45 315 269 264 -3 44 -45 HKL 25 10 100 87 79 -79 189 -174 139 -15 216 -5 159 -158 45 42 316 -71	270 -15 53 -49 123 120 350 -31 42 -38 MKL 10 1 1 420 -41 227 231 400 -20 160 -23 120 -25 MKL 20 1 1 151 145 206 -204 172 -175 172 -174 108 106 80 1 100 -0 160 10	46 -38 116 121 71 76 168 36 H 66 65 278 26 268 1 48 -63 56 -54 168 -6 628 60 105 105 89 87 319 29 HK 17 0 3 288 -33	119-109 - 20 - 23 - 37 - 40 - 77 - 10 - 12 - 13 146 - 4 - 22 - 2 - 24 - 1 - 65 - 52 - 11 - 116 146 - 4 - 22 - 2 - 22 - 3 - 75 - 68 - 109 - 111 118 - 13 - 23 - 12 - 43 - 53 - 46 - 109 - 111 - 118 - 13 - 23 - 12 - 43 - 53 - 46 - 109 - 111
136 127 21* 0 342 348 31* -46 20* -32 17* -13	30 17 27* 28 93 85 HKL 13 1 2 7* 77	200 15 168 168 219 233 370 21	96 100 240 22 109 109 270 -22 77 -73
137 -125 51 -40 267 275 42* 27 139 41 xtc.11	113 -113 29* -26 51 51 100 *7 29* -14	72 -76 44 -35 58 63 169 164	210 29 78 -81 133 -131 HKL 10 1 5 164 -161
244 242 106 107 92 -92 13* 11 18* -2 18* -1	20* -4 17* -23 40* -391 11* -11 MKL 21 1 2	21* 8 20* -14 43 -36 283 276	149 159 96 93 270 10 57 -71 133 -130
290 -306 90 -91 140 167 72 -07 127 -131 53 53	242 -254 17* 4 288 254 45 -42 6* 72	45 -46 87 84 69 -65 481 1 4	81 -71 290 -24 270 7 5 7 -71 133 -130
21ª 3 580 -35 79 -46 240 32 130 -16 120 -115	152 155 223 -217 136 133 169 -168 34 -26	75 74 100 106 41 -40 218 -5	109 100 113 117 HKL 2 1 5 249 -21 279 -16
62 56 16° 20 410 26 436 -46 341 -351 117 111	199 -205 MGL 0 0 2 134 127 139 142 320 32	218 27 152 147 248 -11 158 10	520 35 249 0 289 24 229 -20 HKL 21 0 5
166 -166 44* 50 51 53 440*, 7 131 -134 172 -158	113 -113 1348 1276 58 -44 119 -116 247 237	248 6 288 -52 66 -62 248 -12	122 -121 40 -37 209 9 229 -1 108 -106
164 164 54* 50 51 73 -48 130 -134 77 -22 210 -214	220 -8 110 1 46 -47 239 -21 14* 28	55 -60 107 98 91 93 30 23	58 60 159 -4 33 -35 229 -2 179 4
24 -27 ML 10 0 0 100 80 143 139 40 -32 239 -231	45 49 22# -12 88 85 49 -51 25# -39 59 -59 394 -374 104 -100 61 46 91 -88 150 -151 352 -55 116 115 97 -94 43# 38 24# 21 343 -348 89 88 148 -155 114 -119	26* * 37* 52 76 75 30 -16	519 509 279 276 56 -55 148 -143 200 -35
246 290 247 -247 240 -38 80 -42 336 21 149 144		45 -56 38* -35 121 -123 108 -109	357 356 216 208 220 5 79 -77 206 210
141 -143 52 51 ML 17 10 173 -172 67 -46 33 -25		81 81 22* 3 46 45 50 50	101 -97 68 -72 220 15 210 -1 103 90
212 -218 139 -11 189 -190 - 81 122 -119 111 -103		KL 3 0 3 88 84 67 70 78 -80	91 84 133 131 51 53 59 35 340 35
744 /8 145 74 146 157 158 141 127 130 244 /8 150 74 127 158 152 154 152 155 151 157 158 259 7 131 127 252 223 123 123 123 132 135 151 -55 51 43 231 127 252 -213 153 152 132 -235 255 255 51 43 231 -27 256 -31 158 -51 231 252 255 255	V9 -40 100 100 101 111 133 -140 64 -67 77 -71 100 1145 145 145 84 -76 109 103 112 55 -36 120 120 155 148 226 234 270 -23 55 -70 112 112 134 -137 140 -134 120 120 120 120	•0 37 72 68 66 62 70 68 53 50 63 -66 23# 32 38 43 26# 27 MGL 10 3 26# 27 54 43 15# -2 137 -110 38# 42 98 100 214 -314 50 -63 144 136 43 166	15* 3 41* -46 46 -40 24* 19 91 88 124 -121 17* 18 27* -39 61 -47 30* -15 143 142 MKL 17 1 4 31* 28 101 -100 MKL 22 1 5 33* -23 13* -13* 54 -53 57 -50 50 -55
MRL 4 0 5 1 7 7 8 3 7 7 3 1 7 7 3 1 7 1 3 1 7 1 3 1 7 7 3 1 7 1 3 1 7 7 3 1 7 1 3 1 3 7 1 3 1 3 3 1 3 3 1 1 3 3 3 1 3 3 1 1 3 3 1 1 3 3 1 1 3 3 1 1 3 3 1 <td>HKL 18 0 1 435 457 240 40 104 458 270 8 320 -36 276 -286 380 -20 76 -73 110 -113 73 71 315 333 HKL 7 1 2 280 6 HKL 22 0 2 48 52 60 53 88 -80 330 56 56 0 50</td> <td>10 10 10 10 10 10 10 66 68 244 -3 McL 18 1 73 86 77 -77 274 -20 134 -23 144 9 173 163 194 10 133 -131 105 103 194 -23 48 46 314 27 72 40</td> <td>100 100</td>	HKL 18 0 1 435 457 240 40 104 458 270 8 320 -36 276 -286 380 -20 76 -73 110 -113 73 71 315 333 HKL 7 1 2 280 6 HKL 22 0 2 48 52 60 53 88 -80 330 56 56 0 50	10 10 10 10 10 10 10 66 68 244 -3 McL 18 1 73 86 77 -77 274 -20 134 -23 144 9 173 163 194 10 133 -131 105 103 194 -23 48 46 314 27 72 40	100 100
260 - 273 - 78 - 79 197 - 198 137 120 60 55 320 - 40	89 97 163 -164 142 -141 298 -39 92 -92	47 -12 164 0 85 -87 46 37	19* 5 24* 6 52 42 90 -67 512 518
74 - 70 210 200 144 - 164 72 71 148 2 284 - 12	358 -32 210 210 101 103 KKL 14 0 2 157 154	50 53 204 -207 144 1 288 19	55 57 55 -59 26* 13 60 56 22* 6
530 489 191 - 195 148 - 176 79 - 70 98 89 175 170	89 -89 163 -166 148 14 278 284 308 -11	135 -143 75 -78 197 -203 224 -221	53 -50 36* -21 27* 7 90 -95 22* -7
1280 1306 210 - 9 139 2 113 - 104 105 102 131 - 129	172 -176 283 -296 100 -97 189 -6 248 8	45 -57 188 28 135 136 113 114	23* -15 41 63 HKL 3 0 5 139 -150 160 -159
393 -382 48 33 37* 33 MEL 27 1 0 210 -34 MEL 12 1 1 36 54 210 -13 21* -24 155 -161 74 -70 15* 3 28* 42 19* -10 340 -31 40* -31 137 137 127 124 116 -111 46 71 400 -34 74 48 34 52 45 47	224 22 386 -396 199 196 202 212 409 -48 63 63 309 318 246 -251 70 -69 249 19 639 36 98 100 215 -206 46 -44 344 -350 84 89 79 72 537 -533 141 -140 67 -48	67 55 52 61 176 -180 HKL 2 0 205 211 210 22 83 -83 156 16 150 -157 360 -54 300 6 170 10 320 -33 108 -118 44 50 224 10	23* 5 1e4 -134 124 0 153 -158 161 -158 130 -135 131 -130 20* 3 64 75 164 -163 210 15 134 -137 38 -23 264 22 103 95 61 60 26* 0 18* -7 83 -79 49 -49
314 - 318 79 - 78 34 - 18 133 127 19 -8 105 106	30 33 444 1 1 2 119 100 216 219 28 33	30 100	76 -79 45 -19 87 -91 104 -99 121 123
146 354 120 - 17 HKL 18 0 130 125 37 - 25 472 - 46	53 35 149 -17 135 131 209 15 73 77		152 -143 HKL 18 0 4 92 -91 57 -52 205 -205
146 - 149 45 - 38 398 25 68 -68 115 117 63 - 68	80 78 53 52 66 72 240 245 207 -202		239 -4 239 14 101 103 259 -18 232 242
51 - 42 HKL 11 0 42 45 773 - 144 146 28 276 78	52 -13 129 124 148 -184 38 -45 106 10		244 10 10 103 104 104 104 104 104 104 105 105 105 105 105 105 105 105 105 105
144 155 22* 7 12* 5 27* - 27* 27* 20 11* - 3	23= -2 1008 -973 138 -135 214 20 231 -225	62 -57 65 -74 59 -54 57 56	254 5 304 3 37 -36 155 -142 144 44
454 47* 14* - 11 14* - 11 HKL 21 0 0 36* 4* 151 1-3	161 -151 63 65 486 -502 560 -570 4KL 23 1 2 H	KL 4 1 3 56 -58 HKL 19 0 3 35* -38	47 -38 234 -10 224 17 55 -53 148 20
150 140 4* 40 124 131 31* 31* 31* 51 4* 4* 4*	244 10 175 176 350 358 329 332 99 99	55 -47 MKL 11 0 3 24* -17 36* -47	78 82 91 94 85 -99 HKL 12 1 5 93 -99
7* - 4* 23* 10 37 - 72 41* - 33 54 - 57 4* 4*	H5L 25 11 52 49 98 95 206 196 349 -11	15* -7 27* 19 72 74 55 -45	79 -72 54 -52 47 -75 20 8 138 132
152 157 15* 15 200 201 74 -86 MKL 6 L 1 116 124	92 -40 178 -191 62 -60 246 -7 218 -13	66 64 98 58 72 68 23* -7	51 -30 155 154 258 6 51 53 HKL 1 6 CL 10 0 4 70 -64 137 160 208 11 228 0 154 -163 70 -24 137 160 208 11 228 0 154 -163 70 72 107 -11.6 388 -32 228 21 +1 31 259 3 344 +40 55 50 60 59
138 -138 381 403 76 -82 54 -45 141 -137 19* 2	185 189 149 -151 256 17 153 149 280 -280	T0 7L 54 -59 89 90 79 80 H	
26* -2 87 -87 91 95 110 -105 128 123 45 -38	153 -156 207 216 328 -25 101 -101 318 -18	108 108 92 95 23* -26 22* 14	
14* -10 135 148 218 3 47 43 359 -346 47 33	51 -57 472 -495 130 -124 608 -40 92 91	893 -908 128 -135 57 -54 55 -55	
xxx xx	102 -104 152 156 145 -135 182 -175 44 -52	100 -101 140 -142 128 -133 344 45	100 -12 53 -52 145 -146 207 -414 380 37
	224 -229 38 -43 HKL 8 0 2 228 216 107 -109	86 -88 162 -162 36 31 96 -91	100 -2 05 03 344 30 55 -50 70 84
	177 -186 149 5 146 -5 HKL 15 1 2 130 -135	39 -31 137 139 64 61 259 -28	38 45 125 -120 HKL 4 1 5 244 27 300 20
	55 53 101 -102 28 23 102 102 74 74	105 104 210 -14 61 48 95 94	200 -17 250 246 220 -35 300 -20 85 -89
24 29 137 -143 227 29 30 23 138 138 145 428 43	236 -7 46 48 47 -84 40 -56 152 137	270 - 22 132 123 320 - 40 270 20	00 01 -104 61 -61 74 76 77 -15 186 -18 -14 204 0 64 -71 110 114 88 84 47 -44 224 15 224 25 257 -262 304 -47 60 59 51 67 82 72 91 85 314 -14 40 70 640 348 144 7 18 -14
42 40 186 183 76 49 43 202 -164 421 13 01	142 -140 138 -140 194 -192 722 -752 119 109	49 53 138 - 135 64 47 KKL 3 1 4	
13* 19 97 -103 18* 25 40 40 67 -68 133 -13*	78 -73 230 -19 42 -58 47 -95 68 -73	320 18 130 - 23 65 67 150 2	
209 -224 389 403 17* -2 41 -40 U 10 13 -13*	191 138 346 -25 78 14 42 71 452 42 02	112 - 111 200 25 70 70 110 - 24	
108 - 49 54 - 51 279 - 18 224 215 178 180 257 240	120 -120 290 20 864 -853 81 -85 63 74	14* 4 213 211 56 -45 19* 24	38* 40 15* -8 89 -92 24* -21 16* 4
47 43 143 - 160 ktt 19 10 396 - 384 503 - 505 126 - 128	50 40 49 -43 170 -13 103 -101 316 27	275 -278 190 -182 24* 5 80 -88	39* -58 6* 71 61 -57 27* 11 60 -59
164 162 73 72 54 - 54 1092 1144 52 50 124 - 134	330 -22 57 60 115 108 252 -255 388 32	100 -132 38* -45 HKL 20 1 3 18* 18	162 152 286 287 77 -73 HKL 13 0 5 83 -88
137 - 140 239 24 82 79 432 450 87 - 82 171 171	204 -202 80 -88 141 -141 120 120 144 149	71 -71 155 -14* 80 -79 16* 165	161 -150 42* -38 24* 20 86 -87 HKL 20 6
214 21 179 11 92 98 144 9 46 -45 158 15	221 - 221 HKL 2 0 2 434 426 446 - 467 169 9	320 -21 230 14 173 175 107 -100	22* -11 35* 13 23* 10 105 -113 1** 21
55 60 300 -19 139 -10 39 36 29 15 188 -4	HKL 21 0 1 43 37 45 46 149 151 75 78	280 38 240 -23 125 -127 65 76	3** 27 25* -12 2** -22 1*2 150 22* -10
270 -229 HL 12 0 0 79 88 209 -205 238 -34 126 -127	145 - 149 42 - 34 226 16 146 - 11 259 2	61 -55 240 6 54 -30 79 -82	73* -11 17* 17* 2** 10 65 -75 115 115
38 35 0 -18 375 380 704 -705 44 177 180	229 11 266 242 400 - 397 65 - 65 232 - 227 H	41 5 0 3 HRL 12 1 3 83 -85 161 165	2** -7 63 -62 2** -10 7* -79 173 108
TU <thtu< th=""> TU TU TU<!--</td--><td>23 -37 -37 -368 128 -126 -77 -46 -63 -64 306 313 213 214 107 108 231 -229 -68 -59 146 149 117 122 330 -36 -77 73 105 97 57 53 133 -129 214 -217 277 -274 223 214 128 112 33 -61 00 100 -115 141 -161 -161</td><td>70 -73 35 5 186 -190 190 -207 42 35 124 128 163 -161 130 0 40 189 173 55 57 43 43 55 44 45 39 180 -7 310 3 117 -122 87 48 45 45 124 4 117 -122</td><td>>c >s 16* 9 75 -E5 100 96 103 102 LL 11 1 77 77 32* -28 26* -16 62 56 19* 4 135 -123 252 -253 26* -6 5 -5* 25* -A MKL 20 6 102 -101 83 -80 35* 29*</td></thtu<>	23 -37 -37 -368 128 -126 -77 -46 -63 -64 306 313 213 214 107 108 231 -229 -68 -59 146 149 117 122 330 -36 -77 73 105 97 57 53 133 -129 214 -217 277 -274 223 214 128 112 33 -61 00 100 -115 141 -161 -161	70 -73 35 5 186 -190 190 -207 42 35 124 128 163 -161 130 0 40 189 173 55 57 43 43 55 44 45 39 180 -7 310 3 117 -122 87 48 45 45 124 4 117 -122	>c >s 16* 9 75 -E5 100 96 103 102 LL 11 1 77 77 32* -28 26* -16 62 56 19* 4 135 -123 252 -253 26* -6 5 -5* 25* -A MKL 20 6 102 -101 83 -80 35* 29*
	144 -15 210 216 44 32 43 -45 XE 25 1 2 304 -17 191 202 135 -191 MKL 16 0 2 394 -36 83 -79 231 232 45 45 279 -282 73 -73 312 131 46 44 MHL 0 3 5 45 77 -186	82 81 506 -525 108 -114 120 84 90 85 -65 63 -63 218 226 85 40 28 28 175 170 119 -112 178 5 208 19 110 -101 188 -176	Jo vo 1.0 1.1 J15 111 115 111 12* 1 64 70 HKL 5 5 72 -67 101 107 26* 16 117 -110 67 -69 25* -1 125 125 26* 272 110 -112 20* 4 79 -73 228 24 31 +51 272 -23 91 11 125 -14
MeL 6 0 3 145 -149 240 15 121 114 636 637 329 -39	80 61 38 -29 42 41 79 83 150 127 62 -97 190 -6 157 158 58 59 178 -174 255 8 1222 126 67 73 87 -97 246 3 164 18 124 122 222 -257 55 52 84 87	83 79 149 147 279 55 53 62	104 101 154 149 200 20 170 -10 230 -14
43 -41 139 134 322 317 220 -227 37 +33 71 -45		88 88 60 -62 HKL 21 0 3 209 7	130 -120 323 330 51 -50 420 -52 90 80
144 0 69 -100 180 47 65 -61 30 -19 270 -32		279 -33 46 40 108 -119 HKL 4 3 4	228 225 205 -204 200 26 HKL 16 15 81 78
56 -49 198 195 122 -114 MeL 1 0 1 59 -50 MeL 14 11		41 -64 116 118 219 14 62 -63	130 -129 16 91 350 50 241 258 158 157
U-113 70 -70 #120 0 0 0 100 -2 257 256 752 45 45	43 -42 212 214 53 49 55 52 44 47	137 130 46 35 50 -50 56 47	230 -11 143 -136 210 22 84 -40 MEL 3 1 6
216-212 60 -71 146 -151 26 25 275 -255 153 -153	544 -4 244 16 285 286 272 -264 165 -160	57 51 45 -31 264 275 270 31	56 62 140 -136 220 -2 64 -67 96 100
79 70 177 180 93 95 45 41 979 466 99 100	MRL 22 1 1 45 -33 210 225 48 45 95 -94	44 -53 150 49 127 131 110 -10	111 -108 58 -64 52 43 57 -51 159 -151



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 v 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 for 50% are 0.258 as large in linear dimensions. Below: layer at z=0, atoms at $z\simeq\frac{1}{2}$ on pedestals. Above: layer at $z=\frac{1}{2}$, atoms at $z\simeq\frac{1}{4}$ 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 v 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 v phase is shown in Fig. 2. The v 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 vphase similar to those in the P phase. The secondary net of the v 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 v-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, 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 Zr₄Al₃ (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 v 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. 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,

CLARA BRINK SHOEMAKER AND DAVID P. SHOEMAKER

Table 3. Observed interatomic distances for the v phase (Å)

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

Atam	l CN14	2 CN14	4 CN14	5 CN14	13 CN14	16 CN1+	2+ CN14	26 CN14	28 CN14	29 CM14	6 CN15	18 CN15	20 CN15	21 CK15
1	0.118*	2.418*		2.746	2.867	2.793	2.757		2.889 2.857			2.428*		
4	2,410	2.7+6	2.387* 2.821	2.821					2.768	2.869 2.799	2.920		2.888	2.2:4
13	2.867	2,943		2.356*			2.717		2.421*					
16	2.793					2.295* 2.361*			2.801		2,899	2.944		
24	2.757				2.717		2•359* 2•297*					2.835		
26								2.444* 2.211*			2.804		2.852	
28 29	2 .8 89	2.857	2.869	2.768 2.799	2.421*	2.801					2.465*		2.49.*	2.527*
6	0.200*			2,920		2.899	2,855	2.804	2.465*		2.590*	2.490*	2.597*	
18 20 21	2.420		2.944	2.888		2.0		2.852		2.494* 2.527*	2.597*			
12 22		2.536*	2.644* 2.937	3.196	2,600*		3.279							<u>2.683</u> *
3	2.515	2.577		2 562	2.532)		2.537		2,523					2.717
9	0.000	2.544	2.558	2.547	2 463	2.549	2,565		2.510	2.519		2.737		2.652
10	2.529	2 620	2.577	2.559	2.597	1	4,707	2.616			2.664		2.668	2,654
15	2.466	2.442	<u></u>	2,590	5.221	2.569 2.551		2,598	2.519		2.770 2.664			
23			2.473	2.571			2,561			2.529		2.6-0	2,772	
	Atom	12	22	3	8	9	10	11	14	15	19	23	25	
	1	CN16	CN16	2.515	CN12	CN12	2.530	Chile	CHLZ	2.466	CK12		CKIZ	
	2	2.536* 2.644*	2.937	2.577	2.544	2,558			2,620 2,577	2.442		2.473		
	5 13	3.196	2.600*	2,532	2.562 2.601	2.547	2.463	2.559	2.597	2.590		2.571		
	16 24		3.279	2.537			2.549 2.565			2.569	2.551		2.561	
	26 28				2,523		2.510	2.616		2.519	2.598			
	29			ļ		2,519						2.529		
	6 18						2.737	2.664		2.770	2.664		2.640	
	20 21		<u>2.683</u> *	2.717		2.652		2.667	2.654			.2.772		
	12	2.709*		-	2.758	2.870			2.709					
	22			2.834	<u>2.779</u>	2.824			2,641					
	3		2.834	2.330		0.768			2,402					
	8	2.758 2.779			2 768	2.550			2.386					
	¥ ۱0	2.824			2.750		2_430		,				2.355	
	11	2.709	2.641	2.402	2.422	2.386	, , , ,	5.5%	2.342	2.385	2.314	2.415	~~~~~	ļ
	±. 15	2.651						2.385	2.313		2.387			
	19 23							2.314 2.415		2.387				
	25					. <u>.</u>	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 leastsquares 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 j	for	the	v	pha	ise
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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
		1.401 (1.40)	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
		1.508 (1.47)	1.289 (1.28)
16	Mn(12)	1.623	1.397
	Mn(22)	1.620	1.348
		1.622 (1.55)	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
	MnŠi(14)	1.155
	Si(15)	1.166
	Mn(19)	1.176
	Si(23)	1.172
	Mn(25)	1.166
		1.169 (1.1

The 6-coordinated or major bonds form two noninterconnected 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°).

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 rootmean-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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