The Crystal Structure of the X Phase (Mn,Co,Si)

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The crystal structure of the intermetallic compound Mn₄₅Co₄₀Si₁₅, known as X phase (and also as Y phase), has been determined by direct methods from data collected on an automated single-crystal X-ray diffractometer, and has been refined by least-squares methods to a conventional R index of 0.070, based on 1597 observed reflections. The structure is orthorhombic, space group Pnnm, with lattice constants a = 15.42 (2), b = 12.39 (2), c = 4.74 (1) Å [λ (Mo K α_1) = 0.70926 Å], and with 74 atoms per unit cell; $\rho_{exp} = 7.08$ (14), $\rho_{cal} = 7.12$ g.cm⁻³. In a manner resembling a number of other σ -phase related compounds, the X-phase structure is layered, with two main layers and two subsidiary layers per c-axis repeat. The X-phase structure can be regarded as an extension of the structure types represented by Zr_4Al_3 , MgCu₂(C15), and MgZn₂(C14), in that all four of these alloys can be considered as aggregates of infinite pentagonal antiprism columns (i.e. columns of fused icosahedra) with the maximum number of shared pentagon sides per pentagon (in a 'main layer' perpendicular to the columns) increasing according to the sequence 1,2,3,4 for the alloys Zr₄Al₂, MgCu₂, MgZn₂, and X phase respectively. The percentages of sites with coordination number 12, 14, 15, and 16 in the X phase are, respectively: 63, 5, 5, and 27. After submitting this paper, the authors learned that Yarmolyuk, Kripyakevich & Hladyshevskii [Kristallografiya (1970), 15, 268; Sov. Phys. Crystallogr. 15, 226] obtained, with photographic data (refining only with hk0), an essentially similar structure for the X phase, differing only in values of interatomic distances and site compositions.

Introduction

The existence of the X phase was first revealed by Kuz'ma (1962) in an examination of the 800 °C section of the Mn, Co, Si ternary system at a composition of $Mn_{40-35}Co_{45-50}Si_{15}$, later revised by Kuz'ma and Hladyshevskii (1964) to $Mn_{45-40}Co_{40-45}Si_{15}$. Bardos, Malik, Spiegel & Beck (1966), in an investigation of the 1000°C section of the Mn, Co, Si system, reported a new 'Q phase' at nearly the same composition, $Mn_{45}Co_{40}Si_{15}$, and also reported the existence of a Y phase at a composition near $Mn_{39}Co_{42}Si_{19}$. These authors noted, on the basis of a comparison of powder X-ray diffraction patterns, the probable identity of the Y phase with the X phase.

From a 'Q phase' sample of bulk composition $Mn_{45}Co_{40}Si_{15}$, annealed at 1000 °C and kindly provided by Professor Paul A. Beck, five crystal fragments, apparently identical in structure as indicated by singlecrystal X-ray diffraction photography, were isolated. It was initially assumed that the isolated material was representative of the material we knew as 'Q phase'. However, later comparison of the powder diffraction pattern calculated from the refined structure found for the single-crystal material, with the reported experimentally determined diffraction patterns of X, Y, and

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Q phases, indicated that all the isolated single-crystal material was isostructural with the X phase or Y phase. The correspondence between the calculated pattern and the patterns reported for the X and Y phases is given in Table 1; the calculated pattern is based on cell constants obtained by unconstrained least-squares refinement of diffractometer measurements and on approximate thermal, occupancy, and positional parameters. It was not possible to place the reported Q-phase diffraction pattern in similar detailed correspondence with the calculated pattern; material designated 'Q phase' is evidently a mixture of X phase with one or more additional phases.

The chemical composition of the small single crystals obtained from the bulk sample was determined both by electron microprobe and by wet chemical analysis. An elongated prismatic fragment was isolated from an aggregate of morphologically similar fragments and was examined by single-crystal X-ray photographic methods. The fragment was found to be a single crystal of X phase, elongated in the *c*-axis direction. Electron microprobe analysis of the aggregate, approximately 2 mm in diameter, detected no apparent chemical inhomogeneity and gave a chemical composition of approximately Mn₄₅Co₄₂Si₁₃. A more precise determination of the aggregate's chemical composition, afforded by standard wet chemical techniques, gave Mn_{44,4}Co_{40.0}Si_{15,1}. This composition is in accord with the overall bulk composition of the sample (Mn45 $Co_{40}Si_{15}$) from synthesis, and is within the limits specified for the X phase in the 800 $^{\circ}$ C section. This again leads to the conclusion that the so-called 'Q phase' actually is an, as yet, unidentified mixture of phases,

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with the X phase as one constituent; the possibility that a major portion of the mixture is a previously unidentified phase that might be named 'Q phase' cannot be excluded.

Experimental

Single-crystal Weissenberg and precession photographs indicate that the structure is orthorhombic with systematic extinctions corresponding to space groups Pnnm (D¹²_{2h}, No. 58) and Pnn2 ($C^{10}_{2\nu}$, No. 34). As refinement was satisfactory in the centrosymmetric group Pnnm, no further consideration was given to the lower space group. Table 2 gives the relevant crystal data; the lattice constants were obtained from (unconstrained) least-squares refinement of diffractometer measurements, and the density was measured experimentally with a pycnometer by methanol displacement.

The structure was deduced through the application of the symbolic addition direct sign-determining meth-

od (Karle & Hauptman, 1953; Karle & Karle, 1966), operating on a provisional, visually estimated data set of 347 reflections from Weissenberg photographs of levels l=0, 1, 2. By using the reflections 14,8,1, 232, 952 as origin symbols (plus) with additional reflections 382 and 251 (assigned minus) and by applying the \sum_2 relation, it was possible to generate the signs of 171 other reflections. An E map, taken perpendicular to the c axis (section at z=0), quickly revealed the structure, and later comparison indicated that 77% of the 171 sign assignments were correct. While this percentage is much lower than is usually expected for a successful application of this method, it was surprising that the method worked so easily for a structure of this kind, in which the dense packing of atoms leads to very non-statistical distributions of intensities in reciprocal space. Moreover, only three reciprocal lattice layers were used, since intensities in all other layers are related to these by the layering of the structure. With an irregularly shaped X-phase crystal specimen

Table 1. A comparison of the powder pattern computed from single-crystal data with the patterns of X phase and Y phase*

Line		Calcul	ated	Y pha	ase†	X phase‡			
number	hkl	d(Å)	I(rel)	d(Å)	I(rel)	$d(\text{\AA})$	I(rel)		
0	3 1 0	4.7469	36				• •		
1	130	3.9891	10	3.949	1				
1	320	3.9552	56	• • • •	-				
2	400	3.8543	23	3.849	0.5				
3	230	3.6403	63	3.636	1				
4	420	3.2725	46	3.261	0.2				
5	040	3.0973	13	3.093	0.2				
6	321	3.0369	39	3.036	1				
	140	3.0366	9						
7	141	2-5570	46	2.552	0.5		_		
8	002	2.3701	201	2.373	2	2.383	1		
9	112	2.3018	12	2.315	0.5				
				2.266	0.5				
10	212	2.2285	16	2.231	0.5	2.244	I		
11	531	2.1910	917	2.186	7	2.203	4		
12	251	2.1119	1000	2.090	11	2.127	4		
13	720	2.0752	575	2.069	1	2.079	3		
• •	060	2.0649	1//	2.022	5				
14	160	2.0466	95	2.033	3				
	1 3 2	2.0370	201						
15	322	2.0330	251	2.018	3				
15	402	1.007/	591	1.989	12	1.995	5		
10	112	1.9926	153	1 707	12	1 990	2		
	$\frac{1}{2}$	1.9862	987						
17	631	1.9819	64						
1.	640	1.9776	67						
18	550	1.9315	537	1.927	4	1.940	3		
19	422	1.9196	28	1.899	0.2				
	360	1.9160	40						
	332	1.9086	39						
	810	1.9043	36						
20	042	1.8822	53	1.882	0.2				
21	142	1.8684	49	1.856	2	1.861	2		
	512	1.8579	212						
22	261	1.8384	28	1.819	0.5	1.831	1		
	242	1.8285	31						
	641	1.8251	54						
	460	1.8201	65	1 700	0.5				
23	522	1.7982	17	1./90	0.2				
	740	1.7949	27						

Line		Calcul	ated	Y pha	iseț	X phase‡			
number	h k l	d(Å)	I(rel)	d(Å)	I(rel)	d(Å)	I(rel)		
24	361	1.7764	78	1.775	1		. ,		
25	830	1.7464	27	1.739	0.5				
26	270	1.7250	88	1.723	1	1.727	1		
27	152	1.7023	38	1.695	0.5	1.704	1		
	461	1.6992	21			1.01	•		
	910	1.6969	43						
28	741	1.6786	28	1.673	0.5	1.681	1		
	622	1.6771	17				-		
29	912	1.3797	25	1.378	0.5				
	481	1.3752	34						
30	533	1.3311	125	1.331	2	1.332	2		
31	253	1.3128	153	1.312	2	1.316	3		
32	10 0 2	1.2924	64	1.290	1		-		
33	703	1.2839	123	1.284	2	1.286	3		
34	780	1.2668	134	1.264	3	1.269	3		
35	382	1.2570	179	1.256	3	1.259	4		
36	491	1.2505	33	1.249	1				
37	0 10 0	1.2389	65	1.237	3	1.241	1		
	263	1.2385	13						
	10 6 0	1.2354	14						
38	643	1.2344	16	1.231	2	1.235	1		
	12 1 1	1.2339	51						
39	12 3 0	1.2268	132	1.224	3	1.228	3		
	363	1.219	33						
40	952	1.2112	340	1.210	7	1.211	5		
41	004	1.1851	163			1.184	4		
	11 2 2	1.1842	47						
42	3 10 1	1.1673	26			1.158	3		
	392	1.1597	63						

Table 1 (cont.)

* The Y-phase line given here as 2.090 Å, matching the calculated 2.1119 Å line, is given as 2.190 Å in Bardos *et al.* (1966). In that reference a line at 2.190 is an exception to a monotonically decreasing sequence, and further is associated with an X-phase line at 2.127; therefore, it appears that 2.190 should have been 2.090. Other minor changes in the correspondence between the X- and Y-phase patterns have been made. In general, all calculated lines with an intensity <25 have been deleted, except for those cases where weak lines overlap adjacent lines to produce or change the intensity of an observable line.

† Bardos *et al.* (1966).

‡ Kuz'ma (1962).

Table 2. Crystal data

Composition (chemical analysis)	Weight %	Atomic %
Manganese	46.6	44.4
Cobalt	44.9	40.0
Silicon	8.1	15.1
Systematic absences	0kl:k+l	$\neq 2n$; $h0l:h+l\neq 2n$
Space group	Pnnm, N	No 58, D_{12}^{12}
a	15.417 (2	20) Å
b	12·389 (20)
с	4·740 (Ì	D) ໌
V	905 (4)	Å 3
Ζ	74 atom	s per unit cell
Dexp	7.08 (14)) g.cm ⁻³
D _{calc}	7.12 g.cr	m ⁻³
Radiation	Μο Κα.	0·70926 Å (a1)
Linear absorption coefficient $\mu = 2$	56 cm^{-1}	
Mana alta annul a configuration of the	2 2 1	

Mass absorption coefficient $\mu/\rho = 35.91 \text{ cm}^2\text{g}^{-1}$

(approximately 0.155 mm in the largest dimension and 0.05 mm in the smallest) placed in an arbitrary orientation on a Datex (tape) automated G. E. diffractometer, 2993 intensity measurements were made in a single octant of reciprocal space out to $2\theta = 75^{\circ}$. These measurements were made using Zr-filtered Mo $K\alpha$ radiation and the θ -2 θ scan method, with stationarycrystal stationary-counter background measurements

of 40 sec both at the beginning and the end of each scan. After approximately every 60 measurements, the intensities of the standard reflections 720, 060, and 004 were measured; they showed no significant variation. With the standard deviation of the intensity estimated from $\sigma(I) = [(C + T^2B)/10 + (0.01 I)^2]^{1/2}$ (where T = scanning time/total background time), based on counting statistics plus a 1% instrumental error allowance, the 979 reflections with intensities less than $2.5 \sigma(I)$ were deleted. The least-squares refinement was based on the intensities of 1597 observed independent reflections, excluding 40 very strong reflections with $F_o < F_c$, presumably owing to secondary extinction. Attempts to correct the data for absorption, using either numerical integration or the polyhedron method, were unsuccessful, presumably because of the very complicated shape of the crystal as shown by scanning electron microscope photographs. A spherical absorption correction was applied with $\mu r = 1.3$, corresponding to transmission factors ranging from 0.164 to 0.202.

Refinement

During the initial stages of least-squares refinement, it became apparent that the silicon atoms were not uniformly distributed by substitutional disorder among CN12 positions, but instead were mainly confined to four kinds of such positions, three of which appeared to contain mainly silicon, the fourth containing a significantly smaller proportion of silicon. As only one occupancy factor can be satisfactorily refined for each position, the chemical composition at each site in a ternary alloy cannot be determined from X-ray data alone without certain simplifying assumptions. The composition of the X phase indicates that the 74 atoms of the unit cell comprise 33 manganese, 30 cobalt, and 11 silicon atoms. It was assumed that the 28 atoms corresponding to positions with coordination number greater than 12 were manganese, because in other σ phase related phases 'B' atoms, such as cobalt, are not normally found with coordination number greater than 12. A weighted average scattering factor for the CN12 sites not occupied by silicon was then computed from $f_{\text{CoMn}} = (1/39) (9f_{\text{Mn}} + 30f_{\text{Co}}).*$

The effective multiplicities (containing occupancy factors) for the four atom sites containing silicon were then refined. The scattering factors used for this procedure were $f_{\rm Si}$ for the three sites that appeared to contain mainly silicon, and $f_{\rm CoMn}$ for the one site that initially appeared to contain a lesser proportion of silicon. From the ratio of the refined to the crystallographic multiplicity, the implied chemical composition was computed (Table 3). All scattering factors were taken from the *International Tables for X-ray Crystallography* (1962) and were corrected for the real part of the dispersion correction taken from the same source. (These corrections are not made in $Z_{\rm app}$, listed in Table 3, which was calculated from $m_{\rm obs}$.) The quan-

^{*} This expression was constructed from an erroneous atomic ratio, Mn: Co=9:30, for these sites. the correct expression, based on the actual ratio of 5:30, should have been $(1/35) \times$ $(5f_{Mn}+30f_{Co})$. The two expressions are closely similar, numerically, giving 26.5 and 26.7 respectively for the scattering factor (Z_{app}) at $2\theta = 0^\circ$. The error was found too late for it to be corrected in advance of the final least-squares refinement, but the site compositions given in Table 3, and the m_{obs} value given for CoMnSi, have been adjusted on an electron-count basis.

Atoms ner unit cell	it cell	Si			3.40	3·37			1.80	2.93									11.50		15.5
	s per uni	c	6·86	6.86	3.94	0·54	3.43	3·43	0.17	0.92	3·43								29.58		40.0
	Atom	Mn	J·14	1.14	0.66	0-0	0.57	0-57	0-03	0.15	0.57	4·00	4·00	4·00	4·00	4·00	4·00	4·00	32-92	74.00	44·5
		Z_{app}	26.7	26-7	21.3	16.0	26·7	26.7	15.3	17-4	26.7	25.0	25.0	25.0	25.0	25.0	25.0	25-0	Total	11	Atomic %
		$m_{\rm obs}$	1.0	1.0	0.798 (7)	0.57 (1)	0.5	0.5	0.273 (7)	0.622 (11)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
		m_c	1.0	- 0	1. 0	0.5	0.5	0.5	0.25	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
hase atomic parameters		В	0.42 (2)	0.48 (2)	0.46 (3)	0-48 (8)	0.43 (3)	0-42 (3)	0.52 (12)	0.61(7)	0.43(3)	0.54(3)	0.50 (3)	0.61(4)	0.60 (4)	0.57 (3)	0.50 (4)	0.54(3)			
		Z	0.2428 (4)	0.2354 (4)	0.2536(6)	0	0	0	0	0	0	0	0	0	0	0	0	0			
Table 3. X_{I}		V	0.0858 (1)	0.3980(1)	0.2104 (1)	0.9917(3)	0.0573 (2)	0.3107 (2)	Ť	0.7424 (3)	0-8023 (2)	0.5292(2)	0.8993 (2)	0.2779 (2)	0.2130 (2)	0.3990 (2)	0.5865 (2)	0-9026 (2)			
		×	0-1106(1)	0.1759 (1)	0-3981 (1)	0.2156(3)	0-3607 (1)	0.4986 (2)	() -+	0.3546 (3)	0-2092 (2)	0.0701(2)	0.4728 (2)	0.0551 (2)	0.2360(2)	0-3394 (2)	0.2351(2)	0.0506 (2)	~		
				· 	·	, m	u u		21m		u.	ш	ш	ш	ш	ш	ш	ш			
		Sit	8(4)	8(4)	8(4)	(m) (m)	(<i>a</i>)	4(a)	2(4)	$\overline{\mathcal{A}}(\sigma)$	4(a)	4(<i>p</i>)	4(b)	4(p)	4(<i>p</i>)	4(<i>p</i>)	4(p)	4(g)			
		No.	-	• ~	۰، ا	<u>ب</u> ہ	۰ ۲	~ ~	° 0	16	21	14	19	4	Ś	6	15	18	1		
		Atom	CoMn	CoMn	CoMnSi	Si	CoMn	CoMn	Si	5.0	CoMn CoMn	Mn	Mn	Mn	Mn	Mn	Mn	Mn			
		UN CN	12	15	10	12	12	12	12	15	12	14	. 1	16	16	16	16	16) (

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Table 4. Observed (left column) and calculated (right column) structure factors for the X phase

*='un-observed', (=systematic absence, E=secondary extinction. All marked reflections were omitted from the final least-

squares refinement.

1 770 P ;	1.8.2 2.4.1	9.0.L 4.1.L 7 424 397 1 710 -98	5.1.L A.1.L 7 1010 -62 0 1165 1416 3	7.4.1 A.4.1 A.4.1	9.8.L 10.10.L	11.14.L 11.0.L	a 14.5.1	15.11.4 17.7.1	14.17.1	20.10.L 23.3.L
2 11464 4738 3 3 1191 0 4 4 66575 8478 9	1001 0 6 940 144 1100 141 7 1041 0	8 1041 0 2 2244 -2128 3 904 -38 3-1+1 4 1024 45	1 1440 1547 4 5.2.L 2 1220 -1240 5 714 -125 1 1018 1017 6	A34 916 7 1076 74 A39 -707 5 A51 774 96* -116 4 918 -207	2 1070 223 1 241 251 19.11.1 4 212 231 0 970	1 260 -291 4 642 - 4 445 -363 6 1731 41 5 323 -342 7 1060	413 4 040 151 0 4 1000 -130 118 6 1010 -121	*10 #13 5 541 547 17.1.L	3 467 -430 2	145 310 y 1070 10 1050 01 3 612 376
5 1907 0 1 6 1857 1428 8	445 -5+2 1076 0 7-1-L	n 843 616 5 1110 -87 1 212 -186 6 919 -931 2 844 -816 7 1010 -1	AOD 871 5 648 765	7.5.L 7 275 160	4 1070 146 7 1460 -7 6 1070 146 7 1450 -15 7 747 276 3 375 -3	10 0 533 503 0 734 -	14.6.t	19.17.6 1 0.0 0 347 340 9 348 - 1 769 -719 4 1010 -	26 0 104 341 351 1 244 264 0 124 2 410 391 1	20.11-1 21.4-L 1714 1210 0 103 271 1014 -34 1 340 -325
8 3404 3504	0 A04 -119 1.1.L 1 690 22 510 -99 2 671 678	1 206 -220 # 1070 -44 1 126 240 1 1120 -12 4.2.1	473 43 473 436 1 473 43 4,6,1 7	904 -25 A.7.L	9.4.1 5 1028 - 0 505 510 6 782 -8	-4 1 206 17 1 417 - 59 2 1006 -29 2 448 50 1 1048 91 1 241 -	•56 1 357 -318 - •18 2 484 -684 - 203 1 060 -168 -	1 1014 444 4 444 1 1014 -201 5 1044 2 246 287 6 1108 -	-17 1 251 137) 144 204 18.14.1	070 197 2 058 -44* 1044 -710 3 1094 -197
1 220 162 1	114 -561 + 1014 -24 310 162 5 1124 121	7 999 -160 1 277 273 4 1059 71 2 1075 -1760	1 1171 -1516 4 4.1.L 2 246 273 5	1140 270 2 1740 -62 490 10 1 246 -141 490 11 1 140	7 1170 -100 10.17.L 7 1170 -100 10.17.L 1 920 -10 0 000 -1	50 11.16-L 6 254	112 5 268 -267 228 6 276 -268	15.13.L 511 -510 0 149 -	1 1104 -145 (1 1104 -145 (140 7 1064 -15)	20.12.L 21.4.L 246 -286 0 1202 1244 1034 80 1 117 -124
1 111 111	108+ +31 7 270 -198 242 -244 277 249 2.2.1	1.2.1 4 518 -520 0 025 -045 1 217 719 5 195 -222	14645 5041 + 1144 -1201 7 #20 -10 5 100 -685	10+0 -68 5 746 -749 6 1110 -3 7.6.6 7 1050 -10	5 970 -101 2 231 -1 6 1000 -18 3 114	An 1 477 455 16 2 406 418 13.7.(14.7.L 0 1144 - 174	578 108 2 571 - 2 578 108 2 571 -	512 18.14.1 -4 0 1044 -142	70.13-L
6 981 0 8 7 216 223	1099 0 0 729 -146 1 205 174 1.2.1 2 454 759	2 31075 1125 6 106 -632 1 505 646 7 698 686 6 696 -527 6 1030 -272	6 471 - 681 7 998 - 672 0 5 71297 2628 1 928 7 61511 7	210 177 574 654 4.4.L 678 30 0 1544 -1673	4.10.1 5 1074 -1 0 596 486 1 105 299 10.13.1	n2 4 109+ 43 1 21A 2 109- 109 -	416 2 344 -125 744 1 000 -75	1 399 - 34.14.1 6 177 -	140 114 19.0.L	1 1080 -111 0 425 -440 1 1080 -214
n. ?. L 1 n 60* 37 2	ALO 114 1 010 52 000 74 4 1000 -79 740 -72 5 1100 116	5 1110 225 6 1112 1277 4.1.1 7 292 143 0 414 462	1 1116 1326 0 826 4 1 1 771 -826 4 5.4.1 2 459 -512 5	A01 548 1 1070 14 1100 110 7 1040 -59 282 300 3 381 143	7 748 195 0 115 -1 1 290 129 1 413 4 4 502 160 2 769 -1	16 0 A18 568 6 978	111 5 1020 -119 157 6 1040 -197		-1 2 471 0	1151 0 1 221 -18C
1 1477 7 197 -144 3	850 24 7 L020 10 970 10 8 L140 -21	216 -201 1 A21 -010 2 147 -22A 1.3.1 1 299 -318	1 471 404 4 1041 -1146 4 1 471 404 4 1046 22 7 2 444 159 5 954 -99	440 -25 4 1014 -1118 234 294 5 440 -225 6 1000 -71	5 940 140 1 340 2 6 1700 111 4 207 -2	44 1 245 -315 2 260 73 147 11.1811 13.3.1	174 14.8.1 0 781 -799	1040 -14 2 460 -	14 5 1050 124	1074 -80 n 114 150 1071 0 1 Ast -788
4 107 5 5 5 1101 0 6 99 -19 7	1110 60 1000 33 2.3.1 1010 6 0 1014 -1106	n 122 -246 6 1010 147 2 1042 1212 5 104 -351 3 164 155 6 910 -66	3 571 596 + 361 -257 106# -119 7 661 -802 0 5 93# 120 1	7.7.L 7 290 977 1144 -17 964 57 A.9.L	9.11.1 0 #70 979 10.14.1 1 516 -520 0 755 1	n 548 518 0 1490 -1 1 119 207 1 176 114 7 560 -307 2 770 -	108 2 628 -687 1 247 3 1451 1646 663 4 1020 -240	2 248 257 5 1010 1 1110 240 2 336 300 17.8.1	27 10.1.1	21.1.6 1 A15 -754 0 1210 -106 1 970 -57 21.4.1
7 941 D * 8 107+ -6	1070 -30 1 421 474 2 37418 5013 1.1.1 3 404 104	6 601 497 4.4.4	7 288 355 0 1484 -172 3 1 884 13 5	1070 -150 1 1050 -101 1070 -150 1 1050 10 900 -20 2 1000 -201	7 1405 -1912 1 476 -4 1 447 -485 7 419 -4 4 859 616 1 751 -2	.74 3 644 145 11.19.6 4 606 - 139 0 Abn -A78 5 674	497 6 413 -507 -97	1 1000 201 0 940 1 1021 -1 15.16.1 2 921 -	70 7 10A6 986 841 3 780 -181 945 4 1870 1810	2 1044 161 n 427 404 3 1014 -155 1 544 564 4 1024 -48 2 508 202
0.1.L 1 71+ -82	100 -20 5 1150 151 101 -202 6 22165 241	1 212 255 0 477 527 8 1089 - 19 2 560 - 024 8 1009 115	4.5.1 7 464 178 7 6 41518 6413 1 1030 26 5 1 111 345 4 1118 -75 7	1000 100 1 100 -184 1000 -189 4 107 -76 1000 -189 5 110 157	5 294 -296 . 411 .	12.0.1 11.4.1	0 716 -740 1 410 -467	0 1940 1943 3 1348 -1 1 647 -679 4 1914 7 760 -141 5 1346 -1	358 5 416 -399 49 484 19.7.1	21.2.L 23.9.L 0 605 -409 0 1050 -108
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7 991 A	1.5.L 3 3799E-3713 L1+3 -1143 4 1070 170	• • • • • • • • • • • • • • • • • • •	5.7.6 2 884 -011 5 7 244 -248 1 1080 -193 6	978 -53 5 860 -929 1079 122 4 414 404	9.14.L 2 1177 1 0 190 101 3 286 -	791 6 1004 48 182 7 880 -697 13.6.L 758 0 1640 -	374 -311 3 1000 -161 670 4 1040 -201	1 841 -746 2 918 -73 17.9.L 3 600 -586 D 590	0 256 -222 1 1010 28 594 2 998 173	3 10 4 -1035 2 1170 40 4 478 -447 3 1070 -56
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2 627 59A 3 991 0	843 -910 L 1030 -224 2 225 -143 1-17-L 3 210 -190	* 377 +12 2 629 -704 1 3 539 -495 3-18-1 4 1060 -79	529 -556 7.1.L 5 5.20.L 0 288 171 8	364 -315 4 1134 -61 212 100 5 200 6 980 -62 6 514 557	10.7.1 1 1416 -1	486 12.14.L 3 268 30 0 730 -734 4 976	100 1 050 100	14.15.L 3 652 0 1070 142 4 344	010 5 048 -030 010 377 20.5.L	27.9.1 0 619 -592
5 1050 0 1	105* 22 + 101* 1A 911 925 101*1177 2.18.0	0 1010 -64 1 553 525 4.19.L 2 1201 -1220 0 1010 -223	2270 -21 1 387 341 7 1090 154 2 840 -78 420 385 3 565 525	369 -381 7 234 -304 8:3+L 9:5+L	1 1070 -23 3 1160 -11 2 1045 1057 4 116 3 1140 -27 5 416	41 2 1000 93 6 281 359 3 990 130 990 4 567 -570	283 3 363 397	2 108+ -173	1 115 -512	1 1000 -179 2 1070 -159
0 1141 0 4 1 1070 85 2 1011 0	103* 3 1 360 361 2 340 364	* 108* -10 2 105* -118 * 108* -30 2 105* -118 3 331 350 0	6.7.1 5 1080 25 n 6.7.1 5 920 -2 1 700 -121 6 960 -57 2	1027 1641 0 461 431 884 865 1 505 -543 241 -240 2 43541 5950	4 207 44 6 106+ 3 958 0 6 498 528 11-11-1	-#4 0 104+ 0 102+ 0 1 2104 - 0 102+ 0 1 110	- 31 6 272 239 1922	16.14.1 1 321 0 1054 31 2 301 1 342 340 3 514	342 4 335 -357 299 518 20.4.1	0 1089 -174 1 277 228 2 221 -241
1 1010 98 0 4 1041 0 1	226 -166 4 1044 -61 1074 -146 1004 -47 2.161	0 520 512 4.20.L 1 211 -208 0 1040 18	552 466 7 311 351 3 1041 0 7.7.1	1063 1037 6 594 662 308 605 5 302 -313	7 1078 -8 0 2448 1 791 10.8.1 2 288	51 1 1010 18 3 1730 - 76 2 1070 115 3 1730 - 750 3 1070 -117 5 1672 -	-10 1 714 731	2 110* 13 4 104* 5 10**	109 0 1000 104 01 1 327 302 2 370 -330	22-11-1
0-18-L 3 0 1144 -232 4 1 1921 0	1080 -121 0 275 250 1050 -116 1 1060 150 2 721 -757	3 241 -276 2 1010 235 3.20.L 4.21.L	921 0 47288 8085 8 353 294 1 204 47 1031 0 2 441 47	365 401 7 1044 -214 8.4.L 9.6.L	1 1366 1434 a 968 2 1099 -1 5 618	-17 -17 -17 12-16+L 14-3-L	60 3 627 643 6 999 -154 5 493 524	1 1474 1178 0 1044 2 931 0 1 944	3 304 262 100 4 1054 123	1 549 -521 23.0.L
2 1034 74 3 1051 0 0 4 1094 -213 1	1.14.L 3 1074 A8 402 -436 416 -673 2.20.L	0 1007 65 0 304 269 1 1078 -155 2 1058 -28 5.0.L	6.1.L 3 070 -18 0 4 220E 3478 1 5 220E 3478 1	446 510 0 511 -546 456 521 1 465 -446 590 -598 2 17928-1941	5 1438 1148 11,12,L	1 006 544 1 315 2 976 53 2 244	-82 294 15.9.L 227 0 612 657	* 1007 0 3 102* * 1007 0 3 102* * 1146 1:13 * 846	51 0 342 758 849 1 101+ 118	0 1124 0 1 357 -312 2 1051 0
0.10.L 3 U 1131 0 1 1169 1164	617 -663 1 114+ 187 2 108+ 116	3.21.L 0 801 0 223 215 2 951 0	741 232 6 999 -169 3 521 465 7 1030 -41 4 599 531	298 292 3 405 -418 315 297 4 397 -396 291 362 5 222 -244	10.9.1 2 769 0 425 -466 3 1000 -	177 101 12.17.L 3 1004 108 0 236 159 3 1014		17.1.1 0 1833 0 1020 103 1 200	2 1000 -215 3 1040 105 1847 4 320 248	4 1076 0
3 1205 1323	1170 244 2.21.4 635 -443 0 417 644 227 -131 1 404 147	3 924 -#3 4 4.0.L 4 1011 0 0 1004 -904 3 974 -104 1 691 0 871 0	218 -149 0 277 -210 7 968 -209 1 808 64	103+ 110 7 279 -230 8.5.1 9.7.1	1 734 744 4 1030 2 345 -467 5 1030 3 575 697	-90 2 236 133 14.4.1 3 1099 128 0 2342	5 102+ 85	1 944 -2 2 1044 2 344 346 3 1044 3 999 24 4 1413	177 20.4.L 244 0 718 -710 469 1 673 -661	0 1020 -47 1 417 -388 2 1325 1460
0.27.L 0 1300 1307 1 1111 0 0	1.21.L 3.O.L 602 896 0 641 0	2 45785 4967 7 1124 -4 5 556 -467 5.1.1	6.7+L 5 98+ 120 0 72+ 682 5 914 - 13 1	420 -153 C 483 -543 312 324 1 1807 -1906 358 -335 2 1030 129	5 406 421 0 169 6 225 -323 1 576 -	10 12.18.1 1 205 579 0 106* 107 3 222	-231 0 687 -681 -298 2 968 192	• 460 153 5 1010 -10 18.11. 6 1090 160 0 1285 -	2 227 171 1 721 -715 2 346 -366	3 430 -300 4 1070 -25
2 395 386 1	2.0.L 2 771 0	7 1130 0 0 00 -558 • 2117 20+7 1 354 318 7 980 0 2 2894 2976	748 -05 6 4578 0 3 648 -054 7 1028 75 5 394 -385 7 1028 75 5	025 077 3 1324 -1388 1110 -110 4 361 -142 988 -162 5 1118 -1245	10.10.L 3 303 - 0 1349 1374 4 202 1 279 203 4 114 -	269 2 711 -093 5 1607 512 513 13.0.L 6 321	-75 a 334 a15 -75 a 335 -526 300 5 2220 -23	17.2.1 2 100* 0 227 -203 3 100* 1 236 212	99 20.9.L	23+2+L D 483 -417 1 241 112
1 1100 32	814 0 4 23n4 1 579 498 5 576 -574	8 1100 -154 3 800 33 6 340 -230 6 1.1 3 255 281	381 1.7 7.4.1 6 948 187 0 1445 1567 7 971 -420 1 1159 -1199	999 -158 6 1039 50 475 546 7 534 -053	2 541 -559 3 101+ 201 11-14-1 4 1308 992 0 670	0 1104 0 14,5,L 1 434 -383 0 232	220 0 1101 1057	2 1598 -1510 3 1000 80 18.12. 4 197 -155 0 18.	2 442 -458	2 010 -5#0 3 1090 46
1 422 -337	0 6 676 0	· ·2* 134 6 1821 1264	516 - 527 <u>5</u> 12 - 362		\$ 214 190 1 413 -	100 5 1120 -08 1 1110 170	-213 2 1452 1411	\$ 107+ 277 1 370	321 310	0 1080 93

tity minimized was $\sum w(|F_o|-|F_c|)^2$, using for weights $1/[\sigma(F)]^2$ derived from the previously given expression for $\sigma(I)$. Both an isotropic and an anisotropic model were refined, and the anisotropic model was rejected because of the statistically insignificant decline in the R index that resulted, and because of the likelihood of uncorrected anisotropic absorption effects. The final agreement indices, taken over all observed reflections, were $R_1 = 0.070 = \sum ||F_o| - SF_c|| / \sum |F_o|$ and $R_2 = 0.074 = [\sum w(|F_o|-|SF_c|)^2 / \sum w|F_o|^2]^{1/2}$. The final atomic parameters are listed in Table 3 and the comparisons of F_o and F_c are given in Table 4. (F_o for unobserved reflections and systematic extinctions is given as 0.5 F_{min} .)

Discussion

In a manner resembling a large number of other σ phase related intermetallic compounds in which all interstices are tetrahedral, the X phase structure is layered, with four layers per c-axis repeat. Fig. 1 is a projection of the structure onto the x-y plane; the net at z=0 is indicated by solid lines, the net at z= $\frac{1}{2}$ by broken lines, and atoms at approximately z=0.25 and z=0.75 are indicated by filled-in circles. The size of the circles increases with increasing coordination number of the atoms. The only types of coordination polyhedra found are the ones normally found in various combinations in σ -phase related phases, namely those



Fig. 1. Projection of the X-phase structure onto the x-y plane. The net at z=0 is indicated by solid lines, the net at $z=\frac{1}{2}$ by broken lines. Filled-in circles are atoms at approximately $\frac{1}{4}$ and $\frac{3}{4}$. The sizes of the circles increase with increasing coordination number of atoms.

having the coordinations and idealized symmetries CN12 ($\overline{5}$. $\overline{3}$. 2/m), CN14 ($\overline{12}$. 2. m), CN15 ($\overline{6}m2$), and CN16 ($\overline{4}3m$) (see Shoemaker & Shoemaker, 1968).

Each of the pentagons in the main layers may be regarded as a section through an icosahedral coordi-

Table 5. Interatomic distances

3 12 8 10 16 17 14 4 5 9 15 18 No. 2 6 12 19 CN 12 12 12 12 12 12 15 16 16 16 12 14 16 16 2.302² 2.472² 2.350 2.355² 2.7972 2.747² 2.7272 2.672² 2.708² 2.438 1 12 2.7422 2,302 2.508 2.346² 2,4742 2.560² 2,6122 2.712² 2.7452 2.393² 2.406 2.632 2.758 2 12 2.572² 2.700² 2.686² 2.779² 2.812² 2.762² 2.3252 2.3282 2.784 3 12 2,430 2.3162 2.310 2.759 2.7672 2.7522 2.773 12 2,302 2.393 2.381 2.349 6 2,406 2,325 2.381 2.622^{2} 2.611 2,724 2.816² 7 12 2.623 2.472 2.328 2.345² 2.358 2.639 2.753² 2.686 2.736² 8 12 2.774 2.7712 10 12 2.350 2.345 2.784² 2.775² 2.355 2.358 2.361 2.669 2.669 16 12 2.346 2.749^2 2.759^2 2.743 2.474 2.316 2.349 2.361 2.703 17 12 $\begin{array}{c} 2.941^2 \\ 3.122 \\ 2.940^2 \\ 3.071 \end{array}$ 2.279* 2.941² 2.642* 14 2.560 2.572 2.622 14 2.941² 2.632* 2.839² 19 15 2,612 2.700 2.611 2.639 2,669 2.940² 2.623 3.122 2.903* 2.766* 16 2.797 2.632 2.686 2.753² 2.784² 2.839 4 3.071 2.779 2.759 2.724 2.7752 2.7492 2.903* 2.802* 2.876* 2.747 2.712 5 16 2.825* 2.914* 16 2.727 2.758 2.784 2.767 2.686 2.774² 2.7592 2.802* 9 16 2.672 2.745 2.812 2.752^{2} 2.816² 2.669 2.703 2.642* 2.876* 2.825' 15 2.708 2.762 2.743 2.766* 2.914* 2.874* 18 16 2.773 2.736^{2} 2,771 2,742 Mn Мn Mn Mm Mn CoMn CoMn CoMnSi Si CoMn CoMn Si Si CoMn Mn Mn

The superscript numerals indicate the number of times a distance occurs when reading down, and an asterisk indicates a 'major ligand' distance. The standard deviations given by the refinement range between 0.003 and 0.006 Å.

nation polyhedron centered on one of the atoms of the subsidiary layers or, alternatively, as a section through an infinite pentagonal-antiprism column whose axis passes through atoms of the secondary layers parallel to c. Infinite pentagonal-antiprism columns occur in other tetrahedrally close-packed structures, sometimes combined with infinite hexagonal-antiprism columns (as in P phase and v phase). In the X phase, the coordination polyhedra around all the secondary-layer atoms have pentagonal sections in the main layers, which is also true for the M phase, the μ phase (when viewed along [110]), Zr₄Al₃ (viewed along [110]), and the Friauf-Laves phases MgCu₂ (along [110]) and $MgZn_2$ (along [110]). As regards the association of one pentagon with another within a layer, the X phase is an extension of the previously known structure types. In Zr₄Al₃, every main-layer pentagon shares a side with only one other pentagon; in MgCu₂ every such pentagon has two sides in common with other pentagons, and in MgZn₂ each pentagon is surrounded by, at most, three others (Shoemaker & Shoemaker, 1968). In the X phase, three different types of pentagons are found, which share respectively one, three, and the unusual number of four, sides with surrounding pentagons. This unusual arrangement of atoms in the primary layers is reflected in the unusual secondary-layer tessellation pattern, where, in Schläfli notation, the forms 4.35 and 4.3⁴ are found (Fig. 2). These forms are not among the types discussed by Frank & Kasper (1958, 1959).

The tessellations 4.3⁵ and 4.3⁴ cannot occur with equilateral triangles and squares. As previously pointed



Fig. 2. Secondary-layer tessellation. Distances are given in Å, and the vertical displacements (relative to $z = \frac{1}{4}$) are indicated by plus and minus signs.



Fig. 3. 'Major network' for X phase. Single circles represent atoms on layer z=0; double circles represent atoms on layer $z=\frac{1}{2}$. Single lines represent major ligands between atoms in the same main layer; double lines represent major ligands between atoms in two adjacent main layers, and thus represent two ligands per atom. All atoms are CN16 except those with CN14 or CN15 which are marked accordingly.

out (Shoemaker & Shoemaker, 1969), the triangles formed by the secondary atoms in structures containing pentagons in the main layers are not equilateral, but have one angle of about 70° and two angles of about 55° and the quadrilaterals are rectangles with sides of two different lengths. Thus, a 3⁶ tessellation is formed by four angles of approximately 55° and two angles of 70° (atom 1 in the X phase). A tessellation $3^{4}.4$ (atom 2 in the X phase) is thus possible with 3 angles of approximately 70°, one of about 55°, and one of about 90°; a tessellation $3^{5}.4$ (atom 3 in the X phase) occurs by joining five angles of about 55° and one angle of about 90°. Fig. 2 shows how a secondary net is constructed by combining these three types of tessellations, forming triangles and rectangles of the same type and not very much more distorted than those found in other tetrahedrally close-packed structures. Hence, the coordination polyhedra in the X phase have about the same degree of distortion as those in other tetrahedrally close-packed structures, even though the structure does not fall under the classification scheme described by Pearson & Shoemaker (1969). That scheme covers only those structures whose secondary nets can be generated by two sets of parallel lines, leading to secondary net tessellations of the types 4^4 , 3^6 , $4.3.4.3^2$ and $4^2 \cdot 3^3$ only.

In the X phase, as in other layered phases of this type, atoms in the secondary layer are not confined by symmetry to planes at z=0.25 and z=0.75; atom 1 is displaced downward from z=0.25 by 0.034 Å, atom 2 downward by 0.069 Å, and atom 3 upward by 0.030

Å (all with e.s.d.'s of approximately 0.005Å). These displacements are larger than in most such phases, but comparable to the largest (0.058 Å) found in the v phase (Shoemaker & Shoemaker, 1971). They result in CN12-CN12 interatomic distances as long as 2.508 Å and as short as 2.232 Å, compared to the mean CN12-CN12 distance of 2.37 (1) Å. With this exception, all other X-phase interatomic distances appear normal for phases of this type. Table 5 lists the interatomic distances arranged according to coordination number. The superscript numerals indicate the number of times a symmetrically equivalent distance is found (when reading down), and an asterisk indicates a 'major ligand' distance. In the X phase, 63 % of the atoms have CN12, 5% CN14, 5% CN15 and 27% CN16. These percentages are not too different from those found in the Friauf-Laves-Komura phases, namely 66% CN12 and 33% CN16. This close relationship is also apparent in the secondary net of the X phase (Fig. 2), which could be transformed into a net with only 36 tessellations (such as occurs in the Friauf-Laves-Komura phases) by moving atoms 2 together, towards the symmetry center and atoms 3, farther apart.

Although the relative distribution of the Co and Mn atoms over the various positions could not be established in this study, it is clearly shown that the silicon atoms are not randomly distributed over the CN12 positions in this structure. Three of the nine CN12 positions are predominantly occupied by Si atoms, and one position is almost 50% occupied by Si. As was also found in the v phase (Shoemaker & Shoemaker, 1971), there are no Si atoms present in the first coordination shell around the 'Si only' positions. This may indicate a significant ionic charge on the Si atoms, presumably positive in agreement with the demonstrated small size of the Si atom (the average CN12-CN12 distance in the X phase is 2.372 Å).

Although occupancies of positions assumed not to contain silicon were not refined, the fact that the refined isotropic temperature factors fall within a reasonably narrow range lends support to our assumption that silicon is essentially confined to those four positions.

The requirements of a 'major skeleton' as discussed by Frank & Kasper (1959) are met, in the case of the X phase, by a single, three-dimensionally connected framework (Fig. 3).

Note added on 21 September 1971.

It has now come to our attention that the structure of the X phase has been determined independently by Yarmolyuk, Kripyakevich & Hladyshevskii (1970) from photographic data. These authors obtained the trial structure from Patterson sections, and refined it by hk0 electron-density projections to a final R index of 0.155 for 135 observed hk0 reflections. The structure is essentially the same as that derived by us, but individual differences in positional parameters are as large as 0.13 Å; the largest difference in an interatomic distance is 0.28 Å. All intermediate atoms were assumed to be at z=0.25, and all CN12 positions were assumed to contain the same mixture of Mn, Co, and Si atoms; all other positions were assumed to contain Mn.

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