

TiMnSi₂ and TiFeSi₂ with New Orthorhombic-Type Structure*

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(Received 13 October 1981; accepted 23 February 1982)

Abstract

TiMnSi₂ and TiFeSi₂ have been studied by single-crystal X-ray diffraction analysis. The structure is of a new type with space group *Pbam* and $Z = 12$. TiMnSi₂: $a = 8.703$ (2), $b = 9.541$ (2), $c = 7.765$ (4) Å, $D_x = 4.916$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 10.63$ mm⁻¹, $F(000) = 900$, $R = 0.037$ for 769 independent reflections. TiFeSi₂: $a = 8.6137$ (8), $b = 9.534$ (1), $c = 7.6396$ (4) Å, $D_x = 5.078$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 11.65$ mm⁻¹, $F(000) = 912$. The final weighted $R = 0.057$ for 615 reflections. The same structure is found for: ScMnSi₂, one modification of ScFeSi₂ and NbFeSi₂. This new type of structure is characterized by finite rectilinear chains of Mn(Fe) atoms, each metal atom being surrounded by an Si octahedron. Similar chains but of infinite length are also found in the Mn₅Si₃, V₆Si₅, Zr₄Co₄Ge₇ and ScFeSi₂ types of structures.

Introduction

Markiv (1966) reported that the compounds TiMnSi₂ and TiFeSi₂ have an orthorhombic unit cell. A systematic study of ternary transition-metal silicides (Steinmetz, 1980) has established the existence of another new orthorhombic silicide NbFeSi₂ (Steinmetz, Albrecht, Zanne & Roques, 1975) which was assumed to be isotypic with TiFeSi₂. Furthermore, according to Kotur & Bodak (1980), ScMnSi₂ and one modification of ScFeSi₂ crystallize with the unknown TiFeSi₂ type. In this paper the solution of this type of structure is described.

* TiMnSi₂ has been studied at Nancy and TiFeSi₂ independently at Geneva. At the time the manuscripts were prepared, the authors found that they had isotypic structures and decided to write a joint paper.

Experimental

Alloys with starting compositions equivalent to TiMnSi₂ and TiFeSi₂ were prepared from elements of high purity (99.9%) in an arc furnace, under argon atmosphere. A single crystal of TiFeSi₂ with 70 µm mean diameter was directly isolated from the crushed ingot. In the case of TiMnSi₂ the sample was homogenized at 1473 K in a sealed quartz tube under 1.3 mPa. Single crystals were obtained from the powder by gas transport using SiCl₄ as transport agent (temperature of evaporation zone: 1473 K, temperature of deposition zone: 1423 K). Chemical analysis using a CAMEBAX MBX microprobe indicated that the crystals had a uniform composition corresponding to Ti_{25±0.5}Mn_{25±0.5}Si_{50±1}. The choice of space group, according to the Laue class *mmm* and the conditions limiting possible reflections ($0kl$ $k = 2n$; $h0l$ $h = 2n$), was between *Pba2* and *Pbam*. The lattice parameters, given in Table 4, were obtained by least-squares refinement of the 2θ values of 25 (42) reflections for TiMnSi₂ (TiFeSi₂). Data collection for TiMnSi₂ (TiFeSi₂) was carried out on a Nonius CAD-4F (Philips PW1100) four-circle diffractometer in an ω - 2θ mode with graphite-monochromated Mo $K\alpha$ radiation, out to a limit of $\sin \theta/\lambda = 0.9$ (0.7) Å⁻¹, yielding 1601 (821) independent reflections.† The intensities were corrected for Lorentz-polarization, and in the case of TiFeSi₂ for spherical absorption. 769 (615) reflections with $|F| > 2\sigma_F(3\sigma_F)$ were retained for the solution and the refinement of the structure. The distribution of the $E(H)$ values is normal and corresponds to the theoretical distribution for a centrosymmetric structure. In the first trial the space group *Pbam* was assumed, which was confirmed in the final structural analysis. The structure was solved using

† The crystallographic studies of TiMnSi₂ were carried out in the Laboratoire de Minéralogie et Cristallographie, Equipe de Recherche associée au CNRS n° 162, Case Officielle n° 140, 54037 Nancy CEDEX, France.

Table 1. Atomic coordinates for TiMnSi₂ and TiFeSi₂ (space group *Pbam*)

The equivalent or isotropic temperature factors are expressed as $T = \exp[-2\pi^2 \cdot 10^{-2} U(2 \sin \theta/\lambda)^2]$. The former were obtained from $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

TiMnSi ₂					
		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Mn(1)	8(<i>i</i>)	0.0849 (2)	0.2536 (1)	0.2476 (2)	0.26 (2)
Ti(1)	8(<i>i</i>)	0.3289 (2)	0.0468 (1)	0.2404 (2)	0.33 (2)
Si(1)	8(<i>i</i>)	0.3325 (3)	0.3177 (3)	0.3479 (3)	0.37 (4)
Si(2)	4(<i>h</i>)	0.0371 (6)	0.3773 (6)	$\frac{1}{2}$	0.58 (9)
Si(3)	4(<i>h</i>)	0.1270 (6)	0.0967 (7)	$\frac{1}{2}$	0.69 (9)
Si(4)	4(<i>g</i>)	0.0379 (5)	0.3803 (6)	0	0.35 (8)
Si(5)	4(<i>g</i>)	0.1307 (6)	0.1040 (6)	0	0.37 (8)
Ti(2)	4(<i>g</i>)	0.3320 (3)	0.3204 (2)	0	0.29 (3)
Mn(2)	4(<i>e</i>)	0	0	0.2425 (4)	0.32 (3)
TiFeSi ₂					
		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Fe(1)	8(<i>i</i>)	0.0892 (2)	0.2570 (2)	0.2488 (3)	0.36 (3)
Ti(1)	8(<i>i</i>)	0.3275 (3)	0.0477 (2)	0.2378 (4)	0.42 (4)
Si(1)	8(<i>i</i>)	0.3379 (5)	0.3177 (4)	0.3457 (4)	0.38 (7)
Si(2)	4(<i>h</i>)	0.0386 (9)	0.3778 (7)	$\frac{1}{2}$	0.98 (14)
Si(3)	4(<i>h</i>)	0.1238 (7)	0.0969 (7)	$\frac{1}{2}$	0.48 (13)
Si(4)	4(<i>g</i>)	0.0392 (8)	0.3809 (7)	0	0.37 (13)
Si(5)	4(<i>g</i>)	0.1274 (8)	0.1045 (7)	0	0.64 (14)
Ti(2)	4(<i>g</i>)	0.3329 (5)	0.3207 (4)	0	0.33 (6)
Fe(2)	4(<i>e</i>)	0	0	0.2435 (4)	0.38 (5)

direct methods (Main, Woolfson, Lessinger, Germain & Declercq, 1978). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Least-squares refinement (Sheldrick, 1976; and Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) of 73 (30) structural parameters and anisotropic (isotropic) temperature factors led to $R = \frac{\sum |\Delta F|}{\sum |F_o|} = 0.037$ for TiMnSi₂ and 0.074 ($R_w = 0.057$ with $w = 1/\sigma_F^2$) for TiFeSi₂. * The final positional and thermal parameters are listed in Table 1 and the interatomic distances in Tables 2 and 3.

Isotypic compounds

An evaluation of a powder diffraction pattern of ScFeSi₂, prepared by Dr H. F. Braun, gave ortho-

* Lists of structure factors for TiMnSi₂ and TiFeSi₂ and anisotropic thermal parameters for TiMnSi₂ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36801 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances *d* (Å) up to 3.5 Å and rounded values $\Delta\%$ [$\equiv 100 \times (d - \sum r)/\sum r$] for TiMnSi₂

The atomic radii (*r*) used for Ti, Mn and Si are 1.47, 1.35 and 1.32 Å respectively. E.s.d.'s are given in parentheses. CN: coordination numbers as discussed in the text. The distances are arranged according to increasing *d* values.

<i>d</i>			$\Delta\%$	<i>d</i>			$\Delta\%$	<i>d</i>			$\Delta\%$
Si(1)				Si(4)				Ti(2)			
-1Si(1)	2.362 (4)	-10.6	CN=7	-2Mn(1)	2.307 (3)	-13.6	CN=9	-1Si(4)	2.622 (6)	-6.0	CN=7
-1Mn(1)	2.372 (3)	-11.2		-1Si(4)	2.377 (11)	-10.0		-1Si(4)	2.623 (6)	-6.0	
-1Mn(2)	2.413 (3)	-9.6		-1Ti(2)	2.622 (6)	-6.0		-1Si(5)	2.697 (6)	-3.3	
-1Mn(1)	2.428 (3)	-9.1		-1Ti(2)	2.623 (5)	-6.0		-2Si(1)	2.702 (3)	-3.1	
-1Ti(2)	2.702 (3)	-3.1		-2Ti(1)	2.697 (4)	-3.3		-1Si(5)	2.708 (6)	-2.9	
-1Ti(1)	2.717 (3)	-2.6		-2Ti(1)	2.711 (4)	-2.8		-1Si(5)	2.726 (6)	-2.3	
-1Ti(1)	2.729 (3)	-2.2		-1Si(5)	2.757 (8)	+4.4		-2Mn(2)	2.936 (3)	+4.1	
-1Si(2)	2.833 (6)	+7.3				-2Mn(1)	2.954 (3)	+4.7			
-1Si(2)	2.886 (6)	+9.3				-2Mn(1)	3.006 (3)	+6.6			
-1Si(3)	2.933 (6)	+11.1				-2Ti(1)	3.180 (3)	+8.2			
-1Si(3)	2.939 (6)	+11.3				-2Ti(1)	3.209 (2)	+9.1			
-1Si(3)	3.006 (6)	+13.9									
				Si(5)							
Si(2)			CN=7	-2Mn(2)	2.413 (4)	-9.6	CN=9	Mn(1)			CN=7
-2Mn(1)	2.326 (3)	-12.9		-1Ti(2)	2.600 (4)	-6.8		-1Si(4)	2.307 (3)	-13.6	
-1Si(2)	2.428 (11)	-8.0		-1Ti(2)	2.697 (6)	-3.3		-1Si(2)	2.326 (3)	-12.9	
-1Si(3)	2.790 (8)	+5.7		-1Ti(2)	2.708 (6)	-2.9		-1Si(1)	2.372 (3)	-11.2	
-2Ti(1)	2.805 (4)	+0.5		-1Ti(2)	2.726 (6)	-2.3		-1Si(5)	2.427 (4)	-9.1	
-2Si(1)	2.833 (6)	+7.3		-1Si(4)	2.757 (8)	+4.4		-1Si(1)	2.428 (3)	-9.1	
-2Ti(1)	2.835 (4)	+1.6		-1Si(5)	3.019 (10)	+14.3		-1Si(3)	2.494 (4)	-6.6	
-2Si(1)	2.886 (6)	+9.3				-1Mn(2)	2.530 (1)	-6.3			
				Ti(1)			-1Ti(1)	2.897 (2)	+2.7		
Si(3)			CN=6	-1Si(5)	2.600 (4)	-6.8	CN=8	-1Ti(1)	2.900 (2)	+2.8	CN=8
-2Mn(2)	2.464 (4)	-7.7		-1Si(4)	2.697 (4)	-3.3		-1Ti(1)	2.931 (2)	+3.9	
-2Mn(1)	2.494 (4)	-6.6		-1Si(3)	2.716 (4)	-2.6		-1Ti(2)	2.954 (3)	+4.7	
-2Ti(1)	2.716 (4)	-2.6		-1Si(1)	2.717 (3)	-2.6		-1Ti(2)	3.006 (3)	+6.6	
-1Si(2)	2.790 (8)	+5.7		-1Si(1)	2.729 (3)	-2.2					
-1Si(3)	2.880 (11)	+9.1		-1Si(2)	2.805 (4)	+0.5		Mn(2)			
-2Si(1)	2.933 (6)	+11.1		-1Si(2)	2.835 (4)	+1.6		-2Si(1)	2.413 (3)	-9.6	
-2Si(1)	2.939 (6)	+11.3	-1Mn(2)	2.897 (2)	+2.7	-2Si(5)	2.413 (4)	-9.6			
-2Si(1)	3.006 (6)	+13.9	-1Mn(1)	2.897 (2)	+2.7	-2Si(3)	2.464 (4)	-7.7			
			-1Mn(1)	2.900 (2)	+2.8	-2Mn(1)	2.530 (1)	-6.3			
			-1Mn(1)	2.931 (2)	+3.9	-2Ti(1)	2.897 (2)	+2.7			
			-1Ti(1)	3.109 (3)	+5.7	-2Ti(2)	2.936 (3)	+4.1			
			-1Ti(2)	3.180 (3)	+8.2						
			-1Ti(2)	3.209 (2)	+9.1						

Table 3. *Interatomic distances* $d(\text{Å})$ *up to* 3.54 Å *and rounded values* $\Delta\%$ $[=100 \times (d - \sum r)/\sum r]$ *for* TiFeSi_2

The atomic radii (r) used for Ti, Fe and Si are 1.47, 1.26 and 1.32 Å respectively. E.s.d.'s are given in parentheses. CN: coordination numbers as discussed in the text. The distances are arranged such that the sequence of the elements and their numbers correspond to the distance table for TiMnSi_2 .

d			$\Delta\%$	d			$\Delta\%$	d			$\Delta\%$
Si(1)				Si(4)				Ti(2)			
-1Si(1)	2.357 (5)	-10.7	CN=7	-2Fe(1)	2.278 (4)	-11.7	CN=9	-1Si(4)	2.594 (8)	-7.0	CN=7
-1Fe(1)	2.339 (4)	-9.3		-1Si(4)	2.370 (9)	-10.2		-1Si(4)	2.617 (8)	-6.2	
-1Fe(2)	2.363 (4)	-8.4		-1Ti(2)	2.594 (8)	-7.0		-1Si(5)	2.635 (8)	-5.6	
-1Fe(1)	2.397 (5)	-7.1		-1Ti(2)	2.617 (8)	-6.2		-2Si(1)	2.642 (4)	-5.3	
-1Ti(2)	2.642 (4)	-5.3		-2Ti(1)	2.663 (6)	-4.6		-1Si(5)	2.717 (8)	-2.6	
-1Ti(1)	2.704 (4)	-3.1		-2Ti(1)	2.674 (6)	-4.2		-1Si(5)	2.728 (8)	-2.2	
-1Ti(1)	2.742 (4)	-1.7		-1Si(5)	2.742 (9)	+3.9		-2Fe(2)	2.908 (4)	+6.5	
-1Si(2)	2.802 (8)	+6.1						-2Fe(1)	2.896 (4)	+6.1	
-1Si(2)	2.892 (8)	+9.5						-2Fe(1)	3.006 (4)	+10.1	
-1Si(3)	2.849 (7)	+7.9				-2Ti(1)	3.145 (4)	+7.0			
-1Si(3)	2.930 (7)	+11.0				-2Ti(1)	3.174 (4)	+7.9			
-1Si(3)	3.036 (7)	+15.0									
Si(2)				Si(5)				Fe(1)			
-2Fe(1)	2.281 (5)	-11.6	CN=7	-2Fe(2)	2.378 (5)	-7.8	CN=9	-1Si(4)	2.278 (4)	-11.7	CN=7
-1Si(2)	2.42 (1)	-8.3		-2Fe(1)	2.415 (5)	-6.2		-1Si(2)	2.281 (5)	-11.6	
-1Si(3)	2.78 (1)	+5.3		-2Ti(1)	2.562 (6)	-8.2		-1Si(1)	2.339 (4)	-9.3	
-2Ti(1)	2.797 (6)	+0.2		-1Ti(2)	2.635 (8)	-5.6		-1Si(5)	2.415 (5)	-6.4	
-2Si(1)	2.802 (8)	+6.1		-1Ti(2)	2.717 (8)	-2.6		-1Si(1)	2.397 (5)	-7.1	
-2Ti(1)	2.823 (6)	+1.2		-1Ti(2)	2.728 (8)	-2.2		-1Si(3)	2.470 (5)	-4.3	
-2Si(1)	2.892 (8)	+9.5		-1Si(4)	2.742 (9)	+3.9		-1Fe(2)	2.569 (2)	+1.9	
				-1Si(5)	2.96 (1)	+12.1		-1Ti(1)	2.864 (3)	+4.9	
								-1Ti(1)	2.864 (3)	+4.9	
Si(3)				Ti(1)				Fe(2)			
-2Fe(2)	2.415 (5)	-6.4	CN=6	-1Si(5)	2.562 (6)	-8.2	CN=8	-2Si(1)	2.363 (4)	-8.4	CN=8
-2Fe(1)	2.470 (5)	-4.3		-1Si(4)	2.663 (6)	-4.6		-2Si(5)	2.378 (5)	-7.8	
-2Ti(1)	2.704 (5)	-3.1		-1Si(4)	2.674 (6)	-4.2		-2Si(3)	2.415 (5)	-6.4	
-1Si(2)	2.78 (1)	+5.3		-1Si(3)	2.704 (5)	-3.1		-2Fe(1)	2.569 (2)	+1.9	
-1Si(3)	2.822 (9)	+6.9		-1Si(1)	2.704 (4)	-3.1		-2Ti(1)	2.857 (2)	+4.6	
-2Si(1)	2.849 (7)	+7.9		-1Si(1)	2.742 (4)	-1.7		-2Ti(2)	2.908 (4)	+6.5	
-2Si(1)	2.930 (7)	+11.0		-1Si(2)	2.797 (6)	+0.2					
-2Si(1)	3.036 (7)	+15.0		-1Si(2)	2.823 (6)	+1.2					
				-1Fe(2)	2.857 (2)	+4.6					
			-1Fe(1)	2.864 (3)	+4.9						
			-1Fe(1)	2.864 (3)	+4.9						
			-1Fe(1)	2.925 (3)	+7.1						
			-1Ti(1)	3.109 (4)	+5.7						
			-1Ti(2)	3.145 (4)	+7.0						
			-1Ti(2)	3.174 (4)	+7.9						

Table 4. *Lattice constants of compounds of* TiFeSi_2 *type*

	Space group $Pbam$ with $a < b$.			Reference
	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	
ScMnSi_2	9.077 (8)	9.854 (8)	7.928 (6)	(i)
ScFeSi_2	8.984	9.739	7.795	(ii)
	8.960 (8)	9.745 (8)	7.829 (8)	(iii)
TiMnSi_2	8.64	9.54	6.92	(iv)
	8.703 (2)	9.541 (2)	7.765 (4)	(v)
TiFeSi_2	8.56	9.53	7.64	(iv)
	8.6137 (8)	9.534 (1)	7.6396 (4)	(v)
NbFeSi_2	8.689 (5)	9.733 (5)	7.576 (5)	(vi)

References: (i) Kotur, Bodak & Kotur (1980). (ii) Kotur & Bodak (1980). (iii) H. F. Brown (1980, private communication). (iv) Markiv (1966). (v) This work. (vi) Steinmetz, Albrecht, Zanne & Roques (1975).

rhombohedral lattice constants, listed in Table 4, which agree with those reported by Kotur & Bodak (1980). Assuming the TiFeSi_2 type of structure for ScFeSi_2 a powder

intensity calculation using the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977) was made and good agreement between calculated intensities and those observed on a Guinier film was found. At this point it should be mentioned that ScFeSi_2 has a second orthorhombic modification of which the structure has recently been determined by Yarmolyuk, Kotur & Grin' (1980). Also for NbFeSi_2 a powder intensity calculation was made and compared with the published list of d values and intensities (Steinmetz, Albrecht, Zanne & Roques, 1975). Except for two weak impurity lines there is good agreement between observed and calculated intensities and consequently the isotypy of NbFeSi_2 with TiMnSi_2 is certain. No calculations have been made for ScMnSi_2 as neither d values nor intensities have been published: however, Kotur & Bodak (1980) state that ScMnSi_2 is isotypic with TiFeSi_2 . In Table 4 the lattice constants of all presently known compounds of the TiMnSi_2 or TiFeSi_2 type are given in the unit-cell setting for $Pbam$ with $a < b$.

Discussion

An idealized projection of the TiMnSi₂ or TiFeSi₂ structure along the *c* axis is shown in Fig. 1(a). The drawing resembles closely the projection of a predicted hypothetical Frank–Kasper structure which is a pentagon-triangle analogue of the hexagon-triangle σ phase with a common secondary network of type 4.3².4.3 [compare with Fig. 6(b) in Shoemaker & Shoemaker (1969)]. However, for four main layers per unit cell ($z = 0, \sim \frac{1}{4}, \frac{1}{2}, \sim \frac{3}{4}$) there are only three secondary layers ($z = 0, \sim \frac{1}{3}, \sim \frac{2}{3}$). Thus the secondary layers are no longer halfway between the main layers.

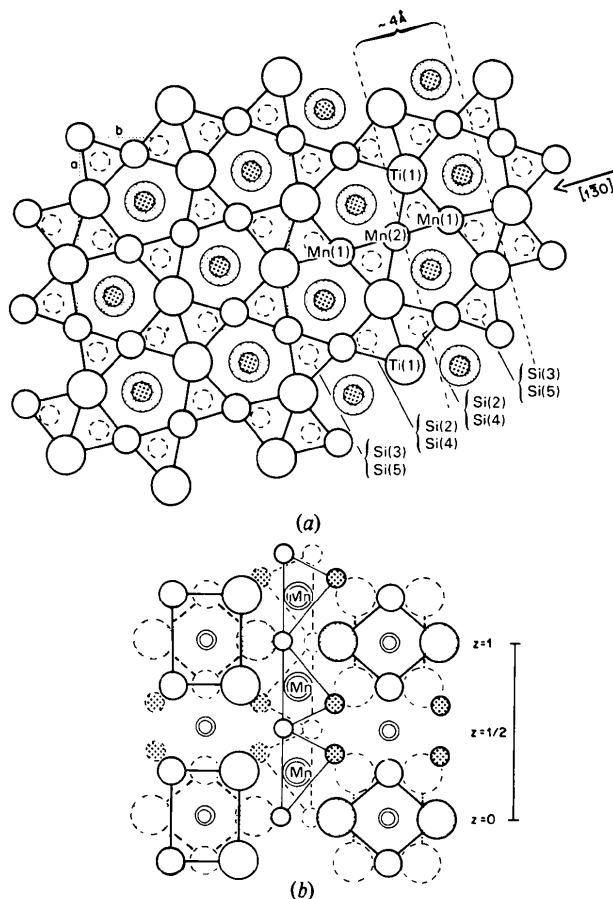


Fig. 1. Idealized projections of the TiMnSi₂-type structure. (a) Projection of the structure along the *c* axis. Large circles: Ti; medium circles: Mn; small circles: Si atoms. Atoms drawn with heavy full lines are at $z \approx \frac{1}{4}$ and $\frac{3}{4}$, atoms drawn with broken lines are at $z = 0$ and $\frac{1}{2}$. The dotted double circles correspond to three superimposed atoms: Ti(2) at $z = 0$ and Si(1) at $z \approx \frac{1}{4}$ and $\frac{3}{4}$. (b) Projection for an ~ 4 Å thick slab of the TiMnSi₂ structure along [130]. The Mn and the Si atoms belonging to the rectilinear three-atom Mn chains and the rectilinear four-atom Si chains aligned along [130] are indicated with double circles for comparison with Fig. 2. Uppermost atoms are indicated with heavy full lines and lowermost with broken lines.

An examination of Tables 2 and 3 shows that many interatomic distances in TiMnSi₂ and TiFeSi₂ are contracted with respect to the sum of the metallic radii of the elements (for a coordination number of 12). The values of $\Delta\%$ (as defined in the legends of Tables 2 and 3) were used to decide whether or not a neighbouring atom should be included in the coordination ($\Delta\%$ negative or when positive ≤ 1.9).

At $z = \frac{1}{2}$ the coordination polyhedra around Si(2) and Si(3) atoms (CN = 7 and 6 respectively) are derived from a trigonal prismatic configuration of metals while at $z = 0$ the coordination polyhedra around Si(4) and Si(5) atoms (CN = 9 in both cases) are derived from a metal, square antiprismatic configuration. Si(2) is surrounded by a trigonal prism of two Mn and four Ti and interacts strongly with another Si(2) through a rectangular face which they have in common in their coordination polyhedron. Si(3) is only surrounded by a trigonal prism of four Mn and two Ti, the next atom in the coordination [one Si(2)] being even further away. As can be seen in Fig. 1(a), the Si atoms at $z = \frac{1}{2}$ are arranged in strings [Si(3)–Si(2)–Si(2)–Si(3)] running approximately along [130] and [130]. It should be noted, however, that Si(3) does not interact as strongly with Si(2) as Si(2) does with its Si(2) neighbour. At $z = 0$, the Si(4)- and Si(5)-centred metal antiprisms share square faces and form columns of four polyhedra in the same directions as defined above. Si(4) is surrounded by an antiprism composed of two Mn and six Ti and interacts with another Si(4) neighbour through the common square face of their polyhedra. The coordination polyhedron for Si(5) is built up from a square antiprism of four Mn and four Ti and also contains another Ti atom outside a square face of the antiprism. The interatomic Si distances in the string Si(5)–Si(4)–Si(4)–Si(5) at $z = 0$ are not equal as is also observed above for the Si string at $z = \frac{1}{2}$.

The Si(1) atoms form dumb-bells parallel to the *c* axis which are in the centre of a 17-atom coordination figure formed by the interpenetration of two 12-atom Frank–Kasper polyhedra (or icosahedra). The pairs of Si(1) are surrounded by six Mn, six Ti and five Si. This coordination figure has already been found in V₇Al₄₅ (Brown, 1959) and is also present in ScFeSi₂ (Yarmolyuk *et al.*, 1980). It should be mentioned that in Zr₄Co₄Ge₇ (Jeitschko, 1969) a 20-fold coordination figure formed by the interpenetration of two 14-atom Frank–Kasper polyhedra is found around the Ge dumb-bells. The ScFeSi₂ and Zr₄Co₄Ge₇ types will be compared later with TiMnSi₂.

An important structural feature in the TiMnSi₂ type is the presence of short interatomic distances between Mn atoms (2.53 Å) which form linear chains of three metals. All Mn atoms (or Fe for TiFeSi₂) are found in the centre of deformed Si octahedra sharing faces and the metals interact between themselves through the common faces of the polyhedra. This surrounding is a

common feature found in $Ti_3Mn_2Si_3$ (Steinmetz, 1980) with the Mn_3Si_3 ternary-type derivative, in $Ti_2Mn_4Si_5$ (Steinmetz & Roques, 1977) a ternary derivative of the V_6Si_5 -type structure, in $Nb_4Fe_4Si_7$ (Jeitschko, Jordan & Beck, 1969) with the $Zr_4Co_4Ge_7$ -type structure and in $ZrFeSi_2$ with the $ScFeSi_2$ -type structure (Yarmolyuk, Kotur & Grin', 1980).

In order to compare the above cited structures with the $TiMnSi_2$ type it is convenient to choose a projection in a direction parallel to the Mn metal chains $[1\bar{3}0]$ and $[130]$. A slab of the $TiMnSi_2$ structure, about 4 Å thick and limited by dashed lines in Fig. 1(a), can be seen in a projection along $[1\bar{3}0]$ in Fig. 1(b). Deformed Si octahedra are indicated around the Mn(1) atoms and the two types of metal square antiprisms around the Si atoms at $z = 0$ and $z = 1$. This structural slab, centred by Mn(1) atoms, is identical, with respect to the poly-

hedral arrangement, to the slab centred by Mn(2) atoms. From Fig. 1(b) the $TiMnSi_2$ structure can be compared with the $Ti_3Mn_2Si_3$, $Ti_2Mn_4Si_5$, $Nb_4Fe_4Si_7$ and $ZrFeSi_2$ structures represented in Figs. 2(a), 2(b), 2(c) and 2(d) respectively. All structures are characterized by rectilinear chains of Mn or Fe atoms which are surrounded by octahedra of Si atoms. All structures drawn in Fig. 2 contain infinite chains of metals. Examination of the drawings shows that with an increasing silicon content, Si-centred (deformed) square antiprisms of metals ($Ti_2Mn_4Si_5$ and $Nb_4Fe_4Si_7$ structures) are first formed and then for 50 at.% Si, Si-centred trigonal prisms (the $ZrFeSi_2$ structure). These trigonal prisms are simply formed by bringing together the metal square antiprisms. For the same silicon content as for $ZrFeSi_2$, the new $TiMnSi_2$ -type structure is found. These two structures, as can be seen in Fig.

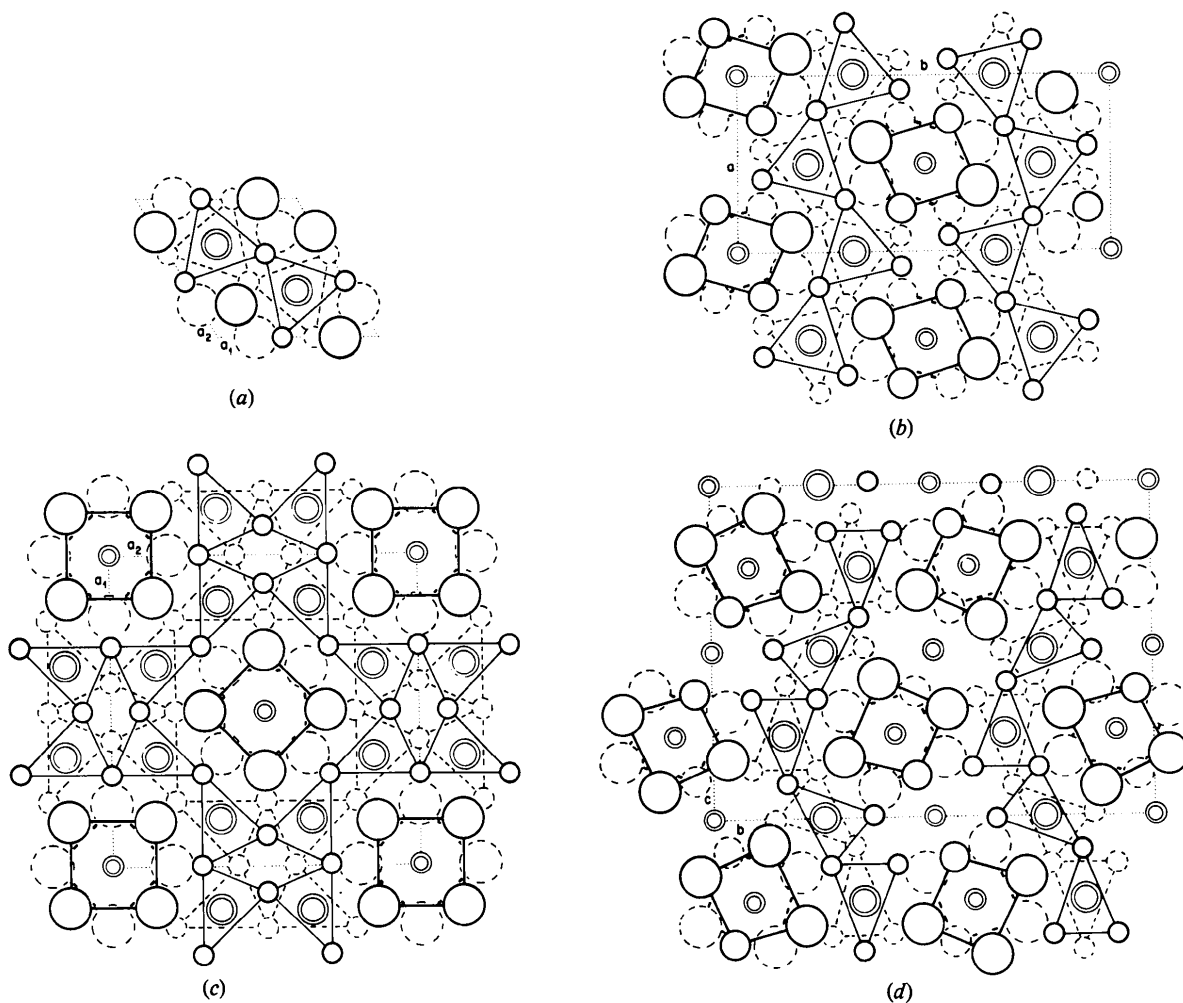


Fig. 2. Structures ($T_xT'_yX_z$) to be compared with $TiMnSi_2$. Large circles: T ; medium (double) circles: T' ; and small (double) circles: X atoms. Atoms drawn with heavy full lines are at $z = \frac{1}{2}$, with broken lines at $z = 0$, with double lines at $z = (\approx) \frac{1}{4}$ and $\frac{3}{4}$. The deformed square antiprisms and octahedra are outlined. (a) $Ti_3Mn_2Si_3$ with Mn_3Si_3 structure-type derivative ($hP16$, $P6_3/mcm$). (b) $Ti_2Mn_4Si_5$ with V_6Si_5 structure-type derivative ($oI44$, $Ibam$). (c) $Nb_4Fe_4Si_7$ with the $Zr_4Co_4Ge_7$ -type structure ($tI60$, $I4/mmm$). (d) $ZrFeSi_2$ with the $ScFeSi_2$ -type structure ($oC96$, $Cmca$).

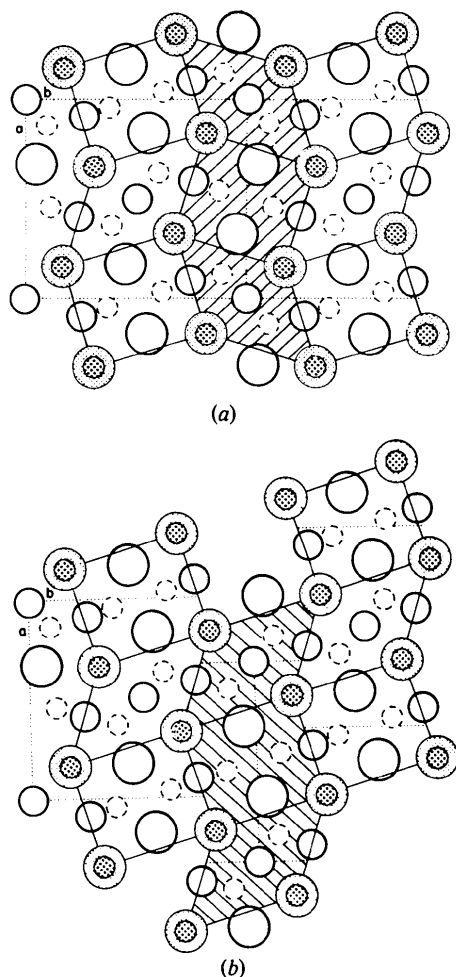


Fig. 3. Formation of infinite metal chains from the TiMnSi₂-type structure. (a) The TiMnSi₂ structure. (b) Shift mechanism to obtain the rectilinear chains of metals.

2(d) and Fig. 1 respectively, are built up with similar Si-centred octahedra and metal square antiprisms arranged in a different but similar way, this arrangement preserving the trigonal prismatic holes where the Si atoms are situated. These common structural features are so propitious that the compound ScFeSi₂ not only crystallizes in its proper ScFeSi₂ type but has a second modification with TiMnSi₂ type. One of the main differences between these structures is found in the metal chains which are infinite and parallel in ScFeSi₂ (ZrFeSi₂) whereas they are finite in length (three atoms) and aligned in two different directions in TiMnSi₂. From these considerations it follows that in Fig. 1(b) the Mn atoms at the vertices of the square antiprisms belong to a metal chain whereas this is no longer true for the Fe atoms at the vertices of the antiprisms shown in Fig. 2(d), although both types of metals are surrounded by Si octahedra.

In Fig. 3, a transformation mechanism is indicated which leads to a change of the two non-parallel three-atom chains into infinite parallel chains and to 'isolated' metal atoms in their Si octahedra. Two operations are performed on TiMnSi₂: a mirror (010) operation on the cross-hatched structural slab shown in Fig. 3(a) and a mutual shift of the three different slabs in the [100] direction as indicated in Fig. 3(b). This hypothetical structure, however, does not correspond to the ScFeSi₂ type. It is a simpler version where all antiprisms have the same orientation.

In the TiMnSi₂- and ScFeSi₂-type structures the Mn or Fe atoms are all surrounded by Si octahedra and all the silicons belong to such polyhedra. This peculiarity suggests a possible description of these two structures based on the octahedral frameworks of the Si atoms, the biggest atoms (Ti or Sc) being located in the holes created in between the octahedra.

This study was supported in part by the Swiss National Science Foundation under Contract 2.001-0.81.

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