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The Crystal Structure of TiFeSi and Related Compounds

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TiFeSi crystallizes with an orthorhombic unit cell of space group $Ima2$ (C_{2v}^{22}) with lattice constants $a = 6.997 \pm 0.002$, $b = 10.830 \pm 0.005$, $c = 6.287 \pm 0.002$ Å. The structure is of a new type, which is a superstructure of the ordered Fe₂P-type, with 12 formula units in the orthorhombic unit-cell. TiFeSi has a strong tendency to form pseudohexagonal multiple twins with the common a axis as twin axis. The structure has been refined by the least-squares method from single-crystal X-ray data, giving a final R value of 0.094 for the 344 observed reflections. TiFeGe crystallizes with the same structure: $a = 7.155 \pm 0.002$, $b = 11.025 \pm 0.007$, $c = 6.405 \pm 0.003$ Å, while TiCoGe is of the ordered Fe₂P-type: $a = 6.222 \pm 0.002$, $c = 3.7267 \pm 0.0010$ Å. The coordination polyhedra in the structures TiFeSi and TiCoGe are very similar to those occurring in TiNiSi (E phase) and Nb₅Cu₄Si₄. The interatomic distances in these structures are discussed.

Introduction

Recent investigations on ternary systems with two transition metals and silicon or germanium showed the

existence of a large number of isotypic phases at the composition 1:1:1 which are called E phases (for a summary of references see Jeitschko, 1968; Jeitschko, Jordan & Beck, 1969), the structure of which was determined for the prototype TiNiSi to be of the ordered PbCl₂-type (Shoemaker & Shoemaker, 1965). In one of these studies (Spiegel, Bardos & Beck, 1963) a

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phase of composition TiFeSi was observed (Spiegel, 1963) which was not isotypic with TiNiSi. This phase was also found independently by Freundlich & Mochai (1966) and Markiv, Gladyshevskij, Skolozdra & Kripjakevič (1967). The latter authors also gave unit-cell data ($6/mmm$, $a=6.24$, $c=6.96$ Å) which are closely related to the unit cell found in the present investigation; they also reported an experimental density of 5.57 g.cm^{-3} for TiFeSi.

The crystal structure of TiFeSi seemed of interest in order to make a comparison with the E phase structure TiNiSi, especially since the ratios of the atomic sizes in TiFeSi are well within the limits found for the occurrence of E phases and therefore cannot be responsible for the change in structure.

Experimental

Samples of TiFeSi were prepared by arc melting the components (all of purity higher than 99.9%) under argon (99.996% Ar) atmosphere. One sample was annealed in an evacuated fused-silica tube at 1000°C for five days. Metallographic examination showed that the sample was about 99% single phase. Powder patterns taken with $\text{Cu } K\alpha$ radiation in a Guinier-de Wolff camera (using one film as filter to absorb fluorescent radiation) gave the same pattern for both the annealed and the unannealed specimen. 'Single crystals' isolated from the crushed samples (annealed and unannealed) showed a strong tendency to twinning, which was not recognized immediately. Single-crystal photographs of such a specimen were taken with a Weissenberg ($\text{Cr } K\alpha$ and $\text{Mo } K\alpha$ radiation) and a Buerger precession camera ($\text{Mo } K\alpha$ radiation) and could be indexed with a hexagonal unit cell of $a=6.29$ and $c=3.50$ Å.

A preliminary intensity calculation gave very good agreement for a structure proposal assuming an ordered Fe_2P -type (Rundqvist & Jellinek, 1959). However, the presence of a number of weak reflections required a doubling of the c axis in agreement with the unit cell found by Markiv *et al.* (1967).

The reciprocal lattice plane ($hk1$) of this larger hexagonal pseudocell, which contains only the weak superstructure reflections (Fig. 1) suggested additionally a doubling of the a axis. A reciprocal lattice based on this unit cell, however, contains a high number of regular extinctions which could not be accounted for by space group extinctions. Therefore, the possibility of twinning (Buerger, 1960) was investigated.

The metallographic examination of a polished and etched (3% HF, 3% HNO_3 , 94% H_2O) specimen using polarized light clearly showed twin boundaries which were not visible under unpolarized light, in addition to normal grain boundaries. The twin boundaries were present both in the annealed and unannealed conditions. Furthermore, the inspection of the pseudo-hexagonal reciprocal lattice plane ($hk1$) mentioned above (Fig. 1), contained some higher angle reflections

which were out of register by up to 0.5 mm. Thus, twinning was clearly established.

The metallographic examination with polarized light revealed that single crystals of dimensions as large as 0.3 mm in diameter were present in the specimens. However, a search for a non-twinned crystal in the crushed samples was not successful.* The closest approximation to a single crystal was a plate-shaped specimen with dimensions $0.20 \times 0.15 \times 0.04$ mm. It contained about 88% of one orientation, while the other two orientations of this multiple twin (trilling) comprised 5 and 7%. These percentages were estimated from the intensity-distribution in the pseudo-hexagonal reciprocal lattice plane ($hk1$) (Fig. 1). The Buerger precession photographs of this specimen showed orthorhombic symmetry for the superstructure reflections, whereas the reflections for the Fe_2P -like subcell still had the pseudohexagonal symmetry. With the lattice constants obtained from these photographs the Guinier-de Wolff powder pattern was indexed and a least-squares fit of the resolved lines (Table 1) gave the following lattice constants using silicon (99.98 Si, $a=5.4311 \pm 0.0004$ with $\lambda\text{Cu } K\alpha_1=1.54051$ Å) as standard:

$$\begin{aligned} a &= 6.997 \pm 0.002 \text{ \AA} & c &= 6.287 \pm 0.002 \text{ \AA} \\ b &= 10.830 \pm 0.005 & V &= 476.4 \pm 0.5 \text{ \AA}^3. \end{aligned}$$

In this setting the orthorhombic a axis corresponds to the twin axis which is also the pseudohexagonal axis of the Fe_2P -like subcell.

For the refinement of the structure intensities were estimated visually with the aid of an intensity strip, which was scaled logarithmically in steps of 10%. The reciprocal lattice planes ($0kl$) to ($3kl$) and ($h, 2l, l$) were recorded from the 88% single crystal mentioned above with a Buerger precession camera ($\text{Mo } K\alpha$ radiation). All symmetry related intensities were measured and averaged after division by the Lorentz-polarization factor. No absorption correction was made. The presence of about 12% of the other two orientations in the specimen did not affect the accuracy

*It is not known whether crushing the brittle samples produced additional twinning by deformation.

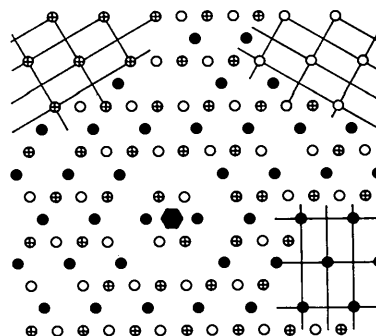


Fig. 1 Three interpenetrating orthorhombic reciprocal lattice planes ($1kl$) of a trilling of TiFeSi, suggesting hexagonal symmetry.

Table 1. Evaluation of Guinier-de Wolff powder patterns of TiFeSi and TiFeGe

		Cu K α radiation					
		TiFeSi			TiFeGe		
hkl*	hkl	d_c (Å)	I_c	I_o	d_c (Å)	I_c	I_o
	110	5.8771	10	vvw	6.0019	2	-
100	{011 5.4372 48}			w, d	5.5382	27	v
	{020 5.4150 21}				5.5125	9	
	121	3.5393	8	vvw	3.6080	1	-
001	{200 3.4985 40}			v	3.5775	73	w
	130	3.2082	3	-	3.2690	1	-
110	{002 3.1435 20}			w, d	3.2025	73	m, d
	{031 3.1306 37}				3.1876	119	
101	{211 2.9421 45}			w, d	3.0051	54	w
	{220 2.9386 26}				3.0009	23	
	112	2.7719	1	-	2.8254	0	-
200	{022 2.7186 19}			v, d	2.7691	9	v, d
	{040 2.7075 8}				2.7562	3	
	141	2.3431	9	-	2.3868	21	-
111	{202 2.3383 302}			v, s, d	2.3861	180	v, s, d
	{231 2.3329 689}				2.3799	456	
	310	2.2801	25	v	2.3311	24	v
	132	2.2453	20	v	2.2877	25	v
201	{222 2.1467 614}			v, s, d	2.1898	704	v, s
	{240 2.1412 263}				2.1834	296	
	150	2.0691	28	v	2.1072	37	v
210	{013 2.0575 252}			v, s, d	2.0961	152	v, s, d
	{042 2.0515 227}				2.0891	125	s, d
	{051 2.0479 237}				2.0849	139	
	321	2.0276	53	w	2.0713	33	v
	330	1.9590	12	v, v	2.0006	14	v, v
	123	1.8824	17	v	1.9180	18	v
	312	1.8457	27	v	1.8847	18	v
300	{033 1.8124 121}			m	1.8461	219	s
	{060 1.8050 56}			w	1.8375	95	w
211	{213 1.7735 88}				1.8085	162	
	{242 1.7697 90}			s, d	1.8040	149	v, s, d
	{251 1.7673 81}				1.8013	137	
002	{400 1.7492 256}			s	1.7887	276	s
	152	1.7283	0	-	1.7603	5	-
	341	1.7012	7	v, v	1.7360	18	v, v
	161	1.6839	8	v, v	1.7148	19	v, v
102	{411 1.6652 2}				1.7022	1	-
	{420 1.6646 2}			v	1.7014	1	-
	332	1.6626	17		1.6967	16	v
	143	1.6126	0	-	1.6428	1	-
301	{233 1.6093 11}			v, v	1.6405	31	w, d
	{260 1.6041 9}			v, v	1.6345	25	
	350	1.5871	0	-	1.6191	1	-
220	{004 1.5717 8}			v, v, d	1.6012	34	v
	{062 1.5653 13}				1.5938	49	w
112	{402 1.5285 2}				1.5617	20	
	{431 1.5270 3}				1.5599	45	w
	114	1.5184	10	-	1.5471	6	-
	170	1.5107	0	-	1.5382	3	-
310	{024 1.5094 20}				1.5377	9	
	{053 1.5061 27}			w, v, d	1.5338	18	w, v, d
	{071 1.5023 24}				1.5294	15	
	323	1.4980	13		1.5284	8	
202	{422 1.4710 6}			v	1.5025	3	-
	{440 1.4693 9}			v	1.5005	4	-
221	{204 1.4337 8}			v, v, d	1.4615	2	-
	{262 1.4288 14}				1.4558	2	-
	352	1.4168	11	v, v	1.4449	5	-
	134	1.4115	0	-	1.4380	2	-
	361	1.3920	10	-	1.4194	3	-
	510	1.3879	9		1.4191	6	-
311	{224 1.3860 56}			m, d	1.4127	21	
	{253 1.3834 58}				1.4097	29	w, d
	271	1.3804	65		1.4063	26	
	172	1.3616	18		1.3865	24	
400	{044 1.3593 63}			w	1.3846	31	w, d
	{080 1.3538 25}			v	1.3781	8	
	343	1.3509	0	-	1.3777	3	-
	163	1.3422	7	-	1.3671	12	-
212	{413 1.3327 117}				1.3606	71	
	{442 1.3311 96}			s	1.3587	53	m, d
	451	1.3301	109		1.3576	64	
	521	1.3245	21	v, v	1.3538	7	-
	530	1.3048	7	-	1.3335	2	-
	181	1.3004	5	-	1.3240	13	-
	314	1.2941	1	-	1.3199	0	-
	370	1.2893	4	-	1.3143	0	-

*Indices of Fe₂P-like subcell

of the intensity measurements of the super-reflections, which are not superimposed in reciprocal space because of the body centered extinctions (Fig. 1). The reciprocal lattice points of the Fe₂P-like subcells of the three orientations of the trilling coincide. However, the orthorhombic distortion of the structure has little influence on the intensities of the subcell and thus the small errors arising through the coincidence of the three pseudohexagonal lattices of the subcell do not affect the structure refinement significantly. Additional data were obtained from an irregularly shaped specimen ($\sim 0.15 \times 0.10 \times 0.10$ mm), which contained nearly equal amounts of each orientation. This specimen was rotated around the pseudohexagonal [100] axis in a Weissenberg camera (multiple-film technique, Mo K α radiation). Three reciprocal lattice layers were evaluated. Only the non-coinciding superstructure reflections and the $h00$ reflections were included in the least-squares refinement, although the intensities of the subcell (divided by 3, to account for the twinning) were utilized to obtain additional scale factors.

Structure determination and refinement

The conditions for possible reflections (hkl only with $h+k+l=2n$, $h0l$ only with $h=2n$ and $l=2n$) lead to the two space groups $Ima2-C_{2v}^{22}$ and $Imam-D_{2h}^{28}$. It was previously mentioned that the intensity calculation for the Fe₂P-type subcell ($P\bar{6}2m$) gave very good agreement with the observed intensities. Therefore, it was concluded that the atomic positions in the four times larger orthorhombic cell would be essentially retained. This corresponds to 12 formula units of TiFeSi in the orthorhombic unit cell with a calculated density of $\rho=5.51$ g.cm⁻³ as compared with the experimental density of $\rho=5.57$ g.cm⁻³, given by Markiv *et al.* (1967). Since the sixfold inversion axis in the Fe₂P-type structure is incompatible with the twofold rotation axis required by $Imam$, this space group could be ruled out. During a least-squares refinement of the Fe₂P-like subcell it was found that the silicon atoms in TiFeSi correspond to the phosphorus atoms and the titanium atoms take the places of the iron atoms in position 3 (g), of the Fe₂P-type structure (Rundqvist & Jellinek, 1959). There are two possibilities for the description of the Fe₂P-type subcell of TiFeSi in space group $Ima2$: one with Ti atoms at $x \approx 0$ and $\frac{1}{2}$, the other with Ti at $x \approx \frac{1}{4}$ and $\frac{3}{4}$. Only the latter could be refined by the least-squares method. A full-matrix program by Busing, Martin & Levy (1962) was used, giving unity weights to all observed structure factors. The values of the atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and were corrected for the real part of the anomalous dispersion (Dauben & Templeton, 1955).

During the first series of least-squares cycles the positional parameters of the atoms, their isotropic temperature parameters and one scale factor were refined. It should be emphasized that a refinement of the scale

factors for individual reciprocal lattice layers was not feasible in this case, since the data for the superstructure and substructure were recorded on different films in the precession camera and the degree found for the orthorhombic distortion of the hexagonal subcell depends to a large extent on the ratio of scale factors for the sub- and superstructure. The incorporation of the Weissenberg data, recorded from the practically ideal trilling mentioned above, however, allowed double checks on the scale factors. All scale factors agreed within 10%.

The refinement of the isotropic thermal parameters gave values for the transition metal atoms varying between $B=0.32 \pm 0.10 \text{ \AA}$ for Ti(3) and $B=0.62 \pm 0.06 \text{ \AA}^2$ for Fe(1). The corresponding values for the lighter silicon atoms were $B=0.74 \pm 0.14 \text{ \AA}$ for Si(1) and $B=0.98 \pm 0.20 \text{ \AA}^2$ for Si(2). These variations were thought to be of no physical significance and it was preferred to fix these parameters with the weighted averages of 0.5 for the transition metal atoms and 0.8 for the silicon atoms in the subsequent refinement cycles. As a test for possible disorder in the structure, occupancy factors were refined together with the positional parameters. The resulting values for occupancy factors varied between 0.98 ± 0.03 for Si(1) and 1.03 ± 0.03 for Ti(3) with the exception of 0.93 ± 0.05 for Si(2) and 1.07 ± 0.03 for Fe(2). Therefore, substantial disorder can definitely be ruled out. There is a slight indication that either Si(2) has a somewhat larger thermal parameter or that this position has a small deviation from full occupancy.

In the final least-squares cycles only the positional parameters and the overall scale factor were varied, resulting in the positional parameters listed in Table 2. The final R value ($R = \sum |F_o - F_c| / \sum F_o$) is 0.094 for the 344 observed structure factors (Table 3). Since this residual value depends mostly on the agreement of the strong subcell reflections, it cannot be taken as a measure for the accuracy of the orthorhombic distorted structure. However, the R value for the 210 observed superstructure reflections is similar: $R=0.096$.

The structures of TiFeGe and TiCoGe

Alloy specimens of these two compounds were prepared in the same way as described for TiFeSi. The Guinier-de Wolff pattern taken with the double-film technique (to absorb fluorescent radiation) and Cu $K\alpha$

radiation showed no impurity lines for the two samples. The annealing treatment (7 days, 840°C in silica tubes) only resulted in a sharpening of the powder lines. The pattern of TiFeGe was very similar to that of TiFeSi, clearly showing the weak superstructure lines of the TiFeSi structure and could be indexed with a similar orthorhombic unit-cell. Least-squares refinement of the lattice constants (as described above) gave $a=7.155 \pm 0.002$, $b=11.025 \pm 0.007$, $c=6.405 \pm 0.003 \text{ \AA}$ and $V=505.3 \pm 0.7 \text{ \AA}^3$. The intensity calculation (Yvon, Jeitschko & Parthé, 1969) using the positional parameters of TiFeSi gave good agreement with the observed intensities (Table 1).

In the Guinier-de Wolff pattern of TiCoGe, on the other hand, no superstructure lines could be observed. It could be indexed with the hexagonal Fe_2P -type unit-cell, giving least-squares refined lattice constants of $a=6.222 \pm 0.002$, $c=3.7267 \pm 0.0010 \text{ \AA}$, $c/a=0.5990 \pm 0.0002$, $V=124.94 \pm 0.12 \text{ \AA}^3$. In the recent literature several ternary compounds with the Fe_2P -type structure have been reported. Some examples are given in Table 4, which also contains the distribution of atoms on the four equipoints of the Fe_2P -type structure. It can be seen that the large transition metal atoms always occupy positions 3(g), whereas the smaller transition metal atoms were found at either the 3(f) sites or at the positions 2(c) and 1(b). Therefore, the atomic distribution, as suggested by the subcell of TiFeSi, was not assumed to be necessarily correct. In order to decide which of the two ordering schemes applied for TiCoGe, relative line intensities were estimated with the aid of an intensity strip and were compared with the calculated intensities for these ordering schemes. The two positional x parameters were varied systematically in these calculations. Agreement between observed and calculated intensities could be obtained only for the atomic distribution and the positional parameters given in Table 4. Thus the atomic order in TiCoGe is the same as in the borides and silicides of Table 4 and corresponds also to the subcell of TiFeSi. A listing of observed and calculated powder intensities of TiCoGe is given in Table 5.

Discussion

A large number of phases have been ascribed the ordered Fe_2P -type structure in the recent literature. Kripjakevič, Markiv & Melnyk (1967) were the first

Table 2. Atomic parameters of TiFeSi and their standard deviations

	Position	x	$\sigma(x)$ ($\times 10^4$)	y	$\sigma(y)$ ($\times 10^4$)	z	$\sigma(z)$ ($\times 10^4$)	B
Ti(1)	4(b)	$\frac{1}{4}$	—	0.2004	7	0.2964	14	0.5 \AA^2
Ti(2)	4(b)	$\frac{1}{4}$	—	0.7793	6	0.2707	14	0.5
Ti(3)	4(b)	$\frac{1}{4}$	—	0.9979	6	0.9178	15	0.5
Fe(1)	8(c)	0.0295	7	0.3764	4	0.1200*	—	0.5
Fe(2)	4(a)	0	—	0	—	0.2501	12	0.5
Si(1)	8(c)	0.0060	13	0.1675	9	0.9953	18	0.8
Si(2)	4(b)	$\frac{1}{4}$	—	0.9747	11	0.5055	23	0.8

* Held constant to fix the origin of the unit cell.

to report the ordering (Table 4) for the four equiatomic phases in the systems {Zr, Hf}-Ni-{Al, Ga}. Analogous positioning of the atoms has been reported for CeNiAl (Table 4) by Dwight, Mueller, Conner, Downey & Knott (1968), who found almost sixty more phases, all at the composition 1:1:1 in the ternary sys-

Table 5. *Calculated and observed intensities of TiCoGe*
Debye-Scherrer camera, Cu K α radiation.
In the low-angle range, data from a Guinier-de Wolff pattern were incorporated.

hkl	d _c (Å)	I _c	I _o	hkl	d _c (Å)	I _c	I _o
100	5.3884	3	2	410	1.1758	11	35
001	3.7267	8	8	321	1.1733	23	3
110	3.1110	19	20	312	1.1658	3	3
101	3.0651	6	6	113	1.1537	5	6
200	2.6942	3	2	203	1.1281	14	13
111	2.3882	56	50	411	1.1214	9	11
201	2.1834	100	100	402	1.0917	5	4
210	2.0366	32	30	500	1.0777	2	-
002	1.8633	29	25	213	1.0605	10	10
300	1.7961	23	20	330	1.0370	4	3
211	1.7872	39	40	501	1.0353	5	10
102	1.7610	0	0	322	1.0301	2	-
301	1.6180	4	3	301	1.0217	1	-
112	1.5955	5	4	420	1.0183	1	-
220	1.5555	8	10	331	.9990	1	-
202	1.5325	1	-	412	.9944	24	30
310	1.4945	3	4	421	.9823	13	15
221	1.4355	0	-	223	.9707	0	-
311	1.3871	7	5	500	.9678	2	2
212	1.3748	16	14	313	.9553	6	4
400	1.3471	4	3	511	.9367	22	20
302	1.2932	16	19	502	.9329	7	15
401	1.2669	0	-	004	.9317	11	3
003	1.2422	0	-	104	.9181	0	-
303	1.2362	1	-	403	.9132	0	-
103	1.2105	1	-	332	.9061	26	25
222	1.1941	8	7				

Table 3. *Observed and calculated structure factors of TiFeSi*

hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c
0 2 0	55	30	1 11 2	39	33	2 4 4	87	93	3 11 4	27	21	7 15 0	<26	7			
0 4 0	60	40	1 13 2	17	20	2 6 4	133	115	3 13 4	21	19	7 17 0	<28	0			
0 6 0	221	191	1 15 2	12	9	2 8 4	82	74	3 15 4	43	40	7 19 0	<49	58			
0 8 0	168	160	1 2 3	45	50	2 10 4	<18	10	3 2 5	60	58	7 21 0	30	34			
0 10 0	115	113	1 4 3	12	8	2 12 4	<171	155	3 4 5	45	39	7 2 1	76	78			
0 12 0	<18	19	1 6 3	39	40	2 14 4	21	18	3 6 5	43	39	7 4 1	27	26			
0 14 0	43	53	1 8 3	24	21	2 16 4	28	28	3 8 5	31	32	7 6 1	58	61			
0 1 1	53	40	1 10 3	31	28	2 1 5	147	181	3 10 5	36	35	7 8 1	57	60			
0 3 1	85	65	1 12 3	44	44	2 3 5	99	104	3 12 5	22	22	7 10 1	57	61			
0 5 1	286	290	1 14 3	46	43	2 5 5	64	69	3 14 5	65	65	7 12 1	32	35			
0 7 1	105	102	1 16 3	25	23	2 7 5	116	119	3 16 5	32	34	7 14 1	59	60			
0 9 1	103	88	1 1 4	41	46	2 9 5	80	83	3 17 5	37	35	7 16 1	<23	18			
0 11 1	104	100	1 1 4	43	43	2 11 5	36	36	3 18 5	62	62	7 18 1	58	62			
0 13 1	94	102	1 5 4	30	30	2 13 5	<21	16	3 19 5	70	70	7 20 1	50	54			
0 15 1	20	27	1 7 4	32	26	2 15 5	5	60	3 20 5	38	40	7 22 1	61	67			
0 17 1	80	53	1 9 4	45	43	2 17 5	6	38	3 21 5	<23	10	7 24 1	67	73			
0 19 1	54	54	1 11 4	28	32	2 19 5	6	68	3 22 5	32	32	7 26 1	30	33			
0 2 2	274	244	1 13 4	<13	8	2 4 6	87	99	3 23 5	21	23	7 28 1	55	54			
0 4 2	83	72	1 15 4	13	16	2 6 6	<18	9	3 24 5	49	53	7 30 1	56	57			
0 6 2	95	91	1 17 4	5	11	2 8 6	75	82	3 25 5	75	82	7 32 1	58	59			
0 8 2	95	92	1 4 5	39	40	2 10 6	29	31	3 26 5	53	53	7 34 1	55	47			
0 10 2	85	89	1 6 5	24	26	2 12 6	44	29	3 27 5	48	48	7 36 1	24	29			
0 12 2	65	78	1 8 5	31	33	2 1 7	18	23	3 28 5	19	22	7 38 1	53	56			
0 14 2	286	257	1 10 5	46	43	2 3 7	71	95	3 29 5	<21	6	7 40 1	63	59			
0 1 3	213	197	1 12 5	23	23	2 5 7	80	88	3 30 5	<22	16	7 42 1	63	15			
0 3 3	102	103	1 14 5	23	24	2 7 7	9	34	3 31 5	29	25	7 44 1	63	15			
0 5 3	94	93	1 1 6	35	33	2 9 7	51	48	3 32 5	26	24	8 0 0	180	178			
0 7 3	167	166	1 3 6	33	36	2 0 8	132	145	3 33 5	40	35	8 2 0	66	59			
0 9 3	419	421	1 5 6	23	23	2 2 8	9	23	3 34 5	29	29	8 4 0	46	46			
0 11 3	22	30	1 7 6	20	20	2 4 8	36	45	3 35 5	35	43	8 6 0	40	42			
0 13 3	77	77	1 9 6	18	22	2 6 8	66	67	3 36 5	32	30	8 8 0	70	70			
0 15 3	99	94	1 11 6	25	25	2 8 8	55	58	3 37 5	24	26	8 10 0	25	26			
0 17 3	182	177	1 13 6	26	27	2 10 8	<21	9	3 38 5	42	41	8 12 0	38	40			
0 19 3	95	96	1 4 7	21	21	2 3 9	22	17	4 4 2	162	156	9 0 0	26	28			
0 2 4	99	94	1 6 7	29	30	2 5 9	79	80	4 8 4	74	62	9 13 0	27	28			
0 4 4	192	177	1 8 7	26	27	2 7 9	37	41	4 1 5	38	40	9 15 0	38	40			
0 6 4	95	96	1 10 7	21	25	2 9 10	47	44	5 3 0	47	60	9 17 0	28	33			
0 8 4	95	91	1 12 7	22	24	2 11 10	51	53	5 5 0	91	104	9 19 0	20	0			
0 10 4	<18	20	1 3 8	26	23	2 13 10	77	72	5 7 0	33	38	9 2 1	46	50			
0 12 4	103	103	1 5 8	30	27	2 15 10	50	41	5 9 0	<20	9	9 4 1	<21	6			
0 14 4	80	74	1 7 8	21	24	2 17 10	56	73	5 11 0	22	30	9 6 1	53	59			
0 16 4	104	104	1 9 8	22	23	2 19 10	54	58	5 13 0	27	35	9 8 1	27	39			
0 18 4	32	38	1 11 8	20	19	2 21 10	<14	3	5 15 0	51	60	9 10 1	53	57			
0 2 5	153	158	1 13 8	26	25	2 23 10	65	46	5 17 0	32	38	9 12 1	<26	24			
0 4 5	79	82	1 15 8	28	30	2 25 10	86	87	5 19 0	<28	9	9 14 1	27	39			
0 6 5	104	96	1 17 8	9	21	11 0	30	34	5 21 0	29	6	9 16 1	<37	22			
0 8 5	118	9	1 19 8	9	21	3 13 0	<20	3	5 2 1	65	74	9 1 2	34	36			
0 10 5	100	101	1 9 10	<22	22	3 15 0	<22	10	4 4 1	13	14	9 3 2	40	46			
0 12 5	68	75	1 11 10	<23	12	3 17 0	<21	15	5 6 1	75	83	9 5 3	37	69			
0 14 5	44	44	1 13 10	<23	9	3 19 0	37	55	5 8 1	28	32	9 7 4	<21	10			
0 1 7	103	101	2 0 0	82	81	3 21 0	28	32	5 10 1	69	67	9 9 4	28	31			
0 3 7	97	85	2 2 0	59	58	3 2 3	54	51	5 12 0	32	32	9 11 4	<22	13			
0 5 7	89	77	2 4 0	98	104	3 4 4	35	35	5 14 1	41	45	9 13 4	<22	18			
0 7 7	54	46	2 6 0	82	82	3 6 4	47	49	5 16 1	21	27	9 15 4	54	51			
0 9 7	118	124	2 8 0	23	22	3 8 4	26	31	5 18 1	25	33	9 17 4	32	36			
0 11 7	17	20	2 10 0	33	38	3 10 4	56	55	5 2 1	48	50	9 19 4	<23	15			
0 13 7	73	75	2 12 0	62	65	3 12 4	47	42	5 3 2	59	67	10 0 0	69	46			
0 15 7	48	36	2 14 0	116	118	3 14 4	55	53	5 4 3	81	96	11 1 0	41	38			
1 3 0	20	19	2 7 1	122	127	3 16 4	26	24	5 4 4	<14	9	11 3 0	33	30			
1 5 0	85	84	2 9 1	126	119	3 18 4	<25	19	5 6 3	64	62	11 5 0	<26	14			
1 7 0	45	5	2 11 1	109	107	3 20 4	3	3	5 7 4	35	41	11 7 0	0	27			
1 9 0	64	51	2 13 1	81	80	3 22 4	5	5	5 8 5	17	15	11 9 0	40	47			
1 11 0	<13	3	2 15 1	78	69	3 24 4	50	56	5 9 4	24	29	11 11 0	<28	21			
1 13 0	22	22	2 17 1	82	80	3 26 4	53	51	5 10 5	27	29	11 13 0	0	28			
1 15 0	40	42	2 19 1	80	82	3 28 4	52	62	5 11 6	20	43	11 15 0	<29	5			
1 17 0	26	27	2 21 1	62	59	3 30 4	<18	10	5 12 7	<20	12	11 17 0	1	38			
1 19 0	27	32	2 23 1	60	61	3 32 4	47	48	5 13 8	38	39	11 19 0	1	25			
1 21 0	<29	19	2 25 1	68	68	3 34 4	52	51	5 14 9	35	39	11 21 0	6	38			
1 2 1	21	19	2 12 2	74	76	3 15 5	28	31	5 15 10	35	39	11 23 0	1	26			
1 4 1	33	30	2 14 2	29	33	3 17 5	24	39	5 16 11	33	35	11 25 0	1	31			
1 6 1	38	39	2 16 2	89	87	3 19 5	24	46	5 17 12	46	51	11 27 0	1	24			
1 8 1	32	34	2 18 2	24	18	3 4 5	<11	5	5 18 13	<24	22	11 29 0	1	38			
1 10 1	45	42	2 1 3	117	122	3 6 7	74	73	5 19 14	<22	22	11 31 0	1	32			
1 12 1	46	41	2 3 3	116	118	3 8 7	19	21	5 20 15	0	1	11 33 0	3	29			
1 14 1	34	35	2 5 3	125	119	3 10 7	66	62	5 21 16	4	64	11 35 0	2	32			
1 16 1	29	28	2 7 3	165	158	3 12 7	37	36	5 22 17</								

(b) Although aluminum is chemically related to boron, silicon and germanium, it is known to behave sometimes like a transition metal. For example, it participates in the formation of such typically inter-transition-metal structures as the σ -phase structure (σ -Nb₂Al and σ -Ta₂Al). This makes the correspondence of the Al atom in ZrNiAl with the Fe atom in NbFeB at least plausible.

(c) In alloys of the large transition metals of the third and fourth group of the periodic system, the elements of the eighth group do frequently occupy the boron positions in structure types, such as CrB, FeB and AlB₂ (for examples, see the compilation by Pearson, 1967) and thus have a coordination of nine nearest neigh-

bours which is also the case for the Ni atoms in CeNiAl and ZrNiAl.

(d) The isotopy of many borides, phosphides, silicides and germanides, on the other hand, (Aronsson, Lundström & Rundqvist, 1965) supports the atomic order of NbFeB and TiCoGe.

The structure of TiFeSi can be derived from the ordered Fe₂P-structure by shifts in the atomic positions of up to 0.4 Å. The interatomic distances, however, are not as much affected by these shifts, since the positions of the neighbouring atoms are adjusted accordingly (Fig. 2). It must be emphasized that the weak superstructure-lines of TiFeSi and TiFeGe are barely visible on Debye-Scherrer films. It therefore seems

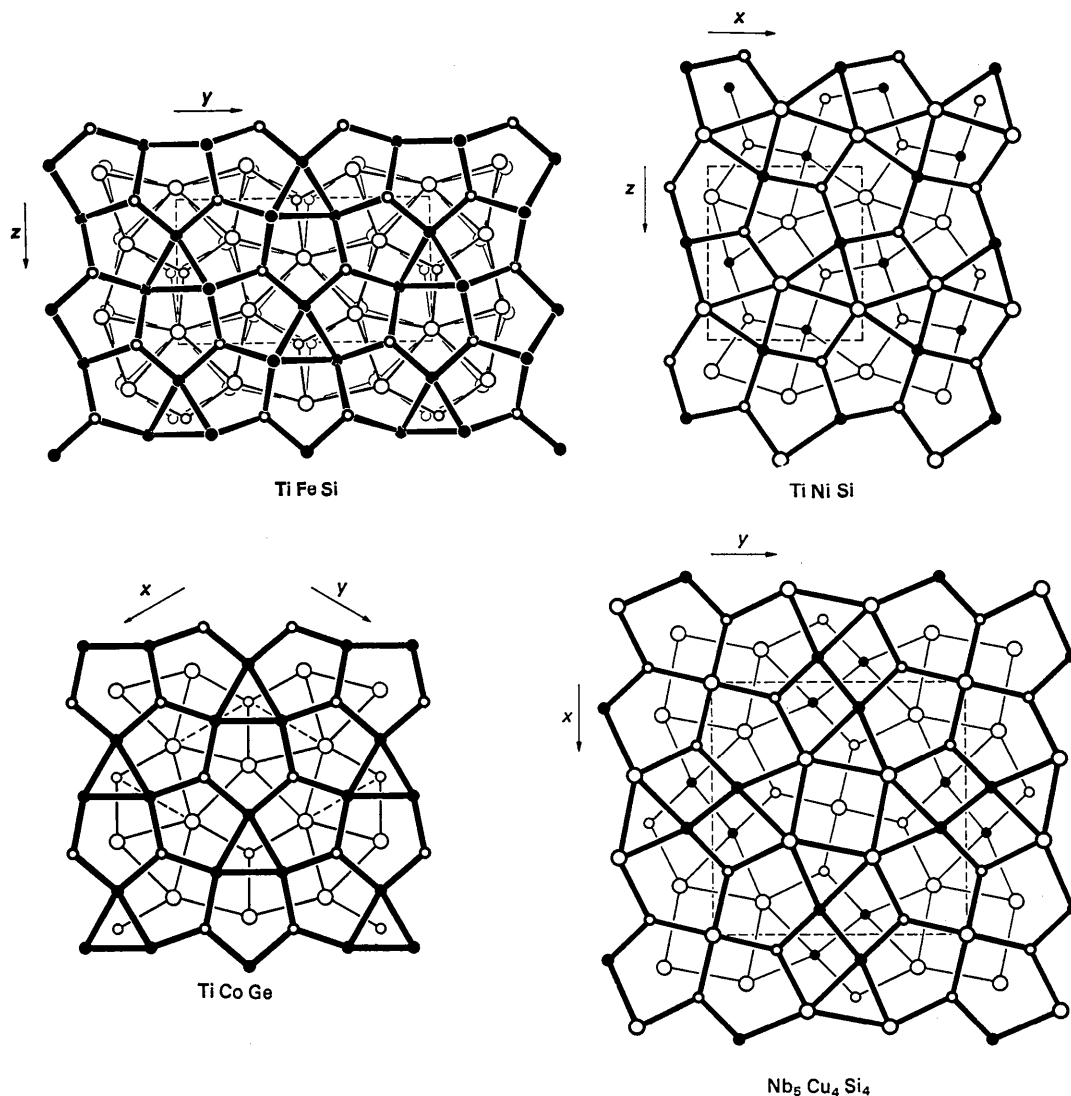


Fig. 2. Projections of the structures TiFeSi, TiCoGe (ordered Fe₂P-type), TiNiSi (ordered PbCl₂-type, *E* phase; setting *Pnma*) and Nb₅Cu₄Si₄. In the projection of TiFeSi the atoms at $x = \frac{1}{2}$ and $x = \frac{3}{2}$ are connected by thin lines; atoms at $x \approx 1$ (connected by thick lines) and $x \approx \frac{1}{2}$ are superimposed. In the structures of TiCoGe, TiNiSi, and Nb₅Cu₄Si₄ atoms connected with thick and thin lines are separated by $\frac{1}{2}$ translation period in the projection direction. Small open circles: Ti, Nb; solid circles: Fe, Co, Ni, Cu; large open circles: Si, Ge

possible that some of the ternary phases, reported to be isotypic with Fe_2P , actually crystallize with the TiFeSi structure. The Guinier-de Wolff pattern of a sample of ZrNiAl (prepared in the same way as TiFeSi), however, contained only lines of the small Fe_2P -type unit-cell, in agreement with the results reported by Kripjakevič *et al.* (1967).

The interatomic distances in TiFeSi (Table 6) show a regularity which has also been observed for the structure of $\text{Zr}_4\text{Co}_4\text{Ge}_7$ (Jeitschko, 1969): all distances transition-metal-silicon (germanium) are shorter than the corresponding sum of the coordination number 12 radii, whereas all distances transition-metal-transition-metal are longer (with the exception of two Ti-Fe dis-

Table 6. *Interatomic distances D (Å) and coordination numbers (CN) in the structure of TiFeSi*

The values are compared with the sum of the atomic radii for CN 12. All distances shorter than 3.9 Å are listed. The values given for CN are the numbers of neighbors within 1.15 (r_A+r_B) and (in brackets) the number of additional neighbors within 1.30 (r_A+r_B).

Ti(1): CN 15(+2)				Fe(2): CN 12			
	D	r_A+r_B	Δ		D	r_A+r_B	Δ
1Ti(3)	3.237 ± 13	2.92	+0.32	2Ti(3)	2.725 ± 11	2.73	0.00
2Ti(1)	3.322 ± 6		+0.40	2Ti(1)	2.803 ± 8		+0.07
1Ti(3)	3.355 ± 12		+0.44	2Ti(2)	2.965 ± 7		+0.24
[2Ti(2)]	3.509 ± 2		+0.59	2Fe(1)	2.691 ± 8	2.54	+0.15
2Fe(1)	2.685 ± 9	2.73	-0.04	2Si(2)	2.390 ± 13	2.61	-0.22
2Fe(1)	2.691 ± 9		-0.04	2Si(1)	2.420 ± 13		-0.19
2Fe(2)	2.803 ± 7		+0.07	2Fe(2)	3.499 ± 2	2.54	+0.96
2Si(1)	2.554 ± 13	2.80	-0.25	Si(1): CN 9(+1)			
2Si(1)	2.574 ± 14		-0.23		D	r_A+r_B	Δ
1Si(2)	2.775 ± 16		-0.02	1Ti(1)	2.554 ± 13	2.80	-0.25
Ti(2): CN 15(+3)				1Ti(3)	2.555 ± 12		-0.24
	D	r_A+r_B	Δ	1Ti(2)	2.557 ± 13		-0.24
1Ti(3)	3.141 ± 11	2.92	+0.22	1Ti(1)	2.574 ± 14		-0.23
2Ti(2)	3.207 ± 4		+0.29	1Ti(3)	2.580 ± 12		-0.22
1Ti(3)	3.245 ± 13		+0.33	1Ti(2)	2.582 ± 13		-0.22
[2Ti(1)]	3.509 ± 2		+0.59	1Fe(1)	2.400 ± 12	2.61	-0.21
2Fe(1)	2.751 ± 8	2.73	+0.02	1Fe(1)	2.413 ± 13		-0.20
2Fe(2)	2.965 ± 7		+0.24	1Fe(2)	2.420 ± 13		-0.19
2Fe(1)	3.123 ± 9		+0.39	[1Si(1)]	3.415 ± 20	2.68	+0.74
2Si(1)	2.557 ± 13	2.80	-0.24	1Si(1)	3.582 ± 20		+0.90
1Si(2)	2.580 ± 16		-0.22	2Si(1)	3.616 ± 11		+0.94
2Si(1)	2.582 ± 13		-0.22	1Si(1)	3.629 ± 21		+0.95
[1Si(2)]	3.217 ± 16		+0.42	1Si(2)	3.779 ± 16		+1.10
Ti(3): CN 15(+2)				1Si(2)	3.881 ± 16		+1.20
	D	r_A+r_B	Δ	Si(2): CN 9(+1)			
1Ti(2)	3.141 ± 11	2.92	+0.22		D	r_A+r_B	Δ
1Ti(1)	3.237 ± 13		+0.32	1Ti(2)	2.580 ± 16	2.80	-0.22
1Ti(2)	3.245 ± 13		+0.33	1Ti(3)	2.604 ± 19		-0.20
1Ti(1)	3.355 ± 12		+0.44	1Ti(1)	2.775 ± 16		-0.02
[2Ti(3)]	3.499 ± 2		+0.58	[1Ti(2)]	3.217 ± 16		+0.42
2Fe(2)	2.725 ± 11	2.73	0.00	2Fe(1)	2.340 ± 10	2.61	-0.27
2Fe(1)	2.782 ± 9		+0.05	2Fe(1)	2.345 ± 12		-0.26
2Fe(1)	3.010 ± 9		+0.28	2Fe(2)	2.390 ± 13		-0.22
2Si(1)	2.555 ± 12	2.80	-0.24	1Ti(3)	3.703 ± 19	2.80	+0.90
2Si(1)	2.580 ± 12		-0.22	2Si(2)	3.499 ± 2	2.68	+0.82
1Si(2)	2.604 ± 19		-0.20	2Si(1)	3.779 ± 16		+1.10
1Si(2)	3.703 ± 19		+0.90	2Si(1)	3.881 ± 18		+1.20
Fe(1): CN 12(+1)							
	D	r_A+r_B	Δ				
1Ti(1)	2.685 ± 9	2.73	-0.04				
1Ti(1)	2.691 ± 9		-0.04				
1Ti(2)	2.751 ± 8		+0.02				
1Ti(3)	2.782 ± 9		+0.05				
1Ti(3)	3.010 ± 9		+0.28				
1Ti(2)	3.123 ± 9		+0.39				
1Fe(2)	2.691 ± 8	2.54	+0.15				
1Fe(1)	2.709 ± 10		+0.17				
[1Fe(1)]	3.086 ± 11		+0.55				
1Si(2)	2.340 ± 10	2.61	-0.27				
1Si(2)	2.345 ± 12		-0.26				
1Si(1)	2.400 ± 12		-0.21				
1Si(1)	2.413 ± 13		-0.20				

tances which are only slightly shorter). A comparison of the interatomic distances in TiNiSi (Shoemaker & Shoemaker, 1965) and Nb₅Cu₄Si₄ (Ganglberger, 1968) shows the same regularity.

The coordination polyhedra for the corresponding atoms in these structures (Fig. 2) are very similar. Each large transition-metal atom (excepting the fifth Nb in Nb₅Cu₄Si₄) has 15 nearest neighbors: 10 transition-metal atoms and 5 silicon or germanium atoms. These tightly bound silicon or germanium atoms form a more or less regular quadratic pyramid in each of these structures. The small transition-metal atom has 12 neighbors: 8 atoms at the corner of a quadrangular prism and 4 more atoms outside the prism side faces. The four tightly bound Si(Ge) atoms of this polyhedron form a tetrahedron in the structures of TiFeSi, TiCoGe and TiNiSi. In Nb₅Cu₄Si₄ one of these four Si neighbours is replaced by a Cu atom at a larger distance. Finally, the environment of the silicon (germanium) atoms is the same in all these compounds: nine transition-metal atoms at a rather short distance, with 6 atoms at the corners of a trigonal prism and 3 atoms outside the rectangular faces of the prism.

The structures of TiFeSi and TiCoGe on the one hand and TiNiSi on the other hand are even more related. The main difference in nearest neighbour environment in these structures arises through the non-equivalence of the Si(Ge) atoms in TiFeSi(TiCoGe): the one Si(Ge) atom in equipoint 8(c) [2(c)] has 6 Ti and 3 Fe(Co) atoms and the other in equipoint 4(b) [1(b)] has 3 Ti and 6 Fe(Co) atoms as nearest neighbors. On the average each Si(Ge) atom has five large and four small transition-metal neighbors as is also the case for the silicon atom in TiFeSi.

The close resemblance of the nearest neighbor environments in these phases is an indication of the stability of these polyhedra. The contraction in the transition-metal-silicon (germanium) distances suggests a strong bond between these elements. The bonding between the transition-metal atoms seems to be of less importance, as is indicated by the stretching of the corresponding distances.

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