The existence of the radiating system 5^6 suggested the possibility of a radiating (3,4)-connected net formed of hexagons which would fill the gap between the plane 5-gon net and the 7-gon, 8-gon, and 9-gon periodic nets. There is in fact a net of this kind (Fig. 15) which consists of an infinite set of concentric tetrahedra linked alternately by lines joining vertices and mid-points of edges. Apart from the central group of 10 3-connected points each successive tetrahedral shell contains 6 3-connected and 4 4-connected points so that for the infinite system $c_3:c_4=3:2$. This net, $R_{3,4}$, completes the family of fundamental nets of Table 2.

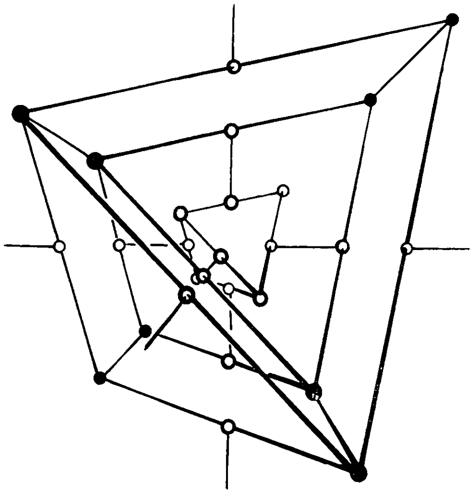

Fig. 15. The radiating net $\{6,\frac{3}{4}\}$.

The relation of the radiating systems and the surface tessellations of part VII to other 4-connected systems is shown below.

Regular and uniform 4-*connected systems*

$y=2$ These include the following:
  $n=3$ octahedron, {3,4}
  $n=4$ plane net, {4,4}
  $n \geq 5$ (*a*) infinite plane radiating nets,
    (*b*) the infinite three-dimensional surface tessellations of part VII, {5,4}, {6,4}, and {7,4}; others have $2\langle y \rangle 3$. (The *y* values for these nets were not given, and {7,4} was not illustrated; it is the reciprocal of Fig. 22(*c*) of part VII).

$y=3$
  $n=3$ finite radiating 3^6 [Fig. 13, (*a*) and (*b*)]
  $n=4$ finite radiating 4^6 [Fig. 13(*c*)]
  $n=5$ infinite radiating 5^6 (Fig. 14)

$y=6$
  $n=6$ diamond net, 6^6 or (6,4).

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A Ternary Alloy with $PbCl_2$-type Structure: TiNiSi(*E*)*

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Beck and coworkers have found *E* phases in several ternary systems of transition elements with either silicon or germanium at the composition 1:1:1. The crystal structure of TiNiSi(*E*) has been determined and refined by least squares with (limited) three-dimensional single-crystal data to a final *R* value of 0·086 (excluding 002 due to apparent extinction, and all non-observed reflexions). The lattice parameters for the primitive orthorhombic cell are:

$$a_0=6{\cdot}1484\pm0{\cdot}0012,\ b_0=7{\cdot}0173\pm0{\cdot}0014,\ c_0=3{\cdot}6698\pm0{\cdot}0007\ \text{Å}.$$

The *E* phase is isotypic with $PbCl_2(C23)$, space group *Pnam*. All near-neighbor distances are within 0·06 Å of the following average values: Ti–Ti 3·18, Ti–Ni 2·83, Ti–Si 2·61, Ni–Ni 2·67, Ni–Si 2·33 Å The numbers of near-neighbors are compared with those in Co_2Si, $\theta-Ni_2Si$ and U_3Si_2.

Introduction

The *E* phase was first identified by Westbrook, DiCerbo & Peat (1958) in the titanium-nickel-silicon system at the composition TiNiSi. Subsequently Spiegel, Bardos & Beck (1963) concluded from the powder X-ray diffraction diagrams that twenty-one additional phases in other ternary systems of transition elements with either silicon or germanium are isomorphous with TiNiSi(*E*) and they indexed the powder patterns on large orthorhombic cells. They found

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* Sponsored by Army Research Office (Durham). Computations were done in large part at the M. I. T. Computation Center.

Table 1. *X-ray powder photographic data for* TiNiSi

WVL*	IOBS	THETA OBS**	H	K	L	THETA CAL	DELTA THETA	ICAL***
3	M	9.648	1	1	0	9.596	0.052	1266
			0	2	0	12.692		238
			0	1	1	13.713		1
			2	0	0	14.523		8
			1	2	0	14.653		139
3	M	15.633	1	1	1	15.556	0.078	1092
			2	1	0	15.889		66
3	VS	19.210	2	0	1	19.094	0.116	2769
			1	2	1	19.197	0.013	4904
3	W	19.486	2	2	0	19.475	0.011	835
3	VS	20.252	2	1	1	20.186	0.065	4090
3	MS	20.653	1	3	0	20.647	0.006	1590
3	VVW	21.902						
3	VVW	22.316						
3	S	23.100	0	3	1	23.006	0.095	2667
			3	1	0	23.070	0.030	1895
3	W	23.201	2	2	1	23.207	-0.006	870
3	M	24.230	1	3	1	24.233	-0.002	1126
3	W	24.431	2	3	0	24.464	-0.033	842
3	S	24.833	0	0	2	24.843	-0.010	2415
3	M	25.787	3	2	0	25.824	-0.037	820
			0	4	0	26.067		123
3	MW	26.339	3	1	1	26.399	-0.060	611
			1	1	2	26.872		153
3	VW	27.230	1	4	0	27.191	0.039	335
3	VW	27.669	2	3	1	27.668	0.001	164
			0	2	2	28.302		49
			3	2	1	28.922		68
			2	0	2	29.293		1
			1	2	2	29.368		33
3	VW(BR)	30.029	3	3	0	30.007	0.022	71
			2	1	2	30.096	-0.067	19
			4	0	0	30.101	-0.072	4
			1	4	1	30.194		6
			2	4	0	30.394		49
			4	1	0	30.892		68
3	M	32.402	2	2	2	32.435	-0.033	313
			3	3	1	32.849		19
			4	0	1	32.939		5
3	MS	33.255	4	2	0	33.199	0.057	420
			2	4	1	33.217	0.038	6
			1	3	2	33.264	-0.009	651
3	VW	33.670	4	1	1	33.692	-0.022	269
3	W	34.272	1	5	0	34.292	-0.020	236
3	MS	35.051	3	1	2	35.065	-0.015	925
			3	4	0	35.340		11
3	M	36.017	4	2	1	35.906	0.111	165
			0	5	1	36.021	-0.004	324
			2	3	2	36.151	-0.135	440
			4	3	0	36.879		6
			1	5	1	36.963		0
3	MS	37.222	2	5	0	37.144	0.078	312
			3	2	2	37.243	-0.021	498
			0	4	2	37.441		80
3	MS	37.925	3	4	1	37.980	-0.055	1188
3	VW	38.378	1	4	2	38.371	0.008	205
			4	3	1	39.481		51
			5	1	0	39.528		21
3	VW	39.684	2	5	1	39.741	-0.057	112
			0	1	3	39.769	-0.086	0
			1	1	3	40.683	0.156	45
3	VW	40.839	3	3	2	40.780	0.059	55
			4	0	2	40.862	-0.024	5
			2	4	2	41.120		42
			0	6	0	41.234		0
			4	1	2	41.560		50
			5	2	0	41.628		103
			3	5	0	41.738		4
			4	4	0	41.821		64
3	M	42.094	5	1	1	42.085	0.009	700
			1	6	0	42.141	-0.047	218
3	M	42.797	2	0	3	42.707	0.090	201
			1	2	3	42.771	0.026	370
3	M	43.350	2	1	3	43.400	-0.051	365
3	M	43.601	4	2	2	43.642	-0.041	359
3	MW	44.254	5	2	1	44.164	0.089	76
			3	5	1	44.274	-0.020	169
			4	4	1	44.355	-0.102	21
3	MW	44.705	1	5	2	44.653	0.053	217
			1	6	1	44.674	0.031	188
			2	6	0	44.848	-0.143	96
			5	3	0	45.093		14
3	MW	45.409	0	3	3	45.330	0.078	316
			2	2	3	45.476	-0.067	98
			3	4	2	45.635		10
3	VW	46.312	1	3	3	46.231	0.081	158
			4	3	2	47.102		6
3	W	47.417	2	5	2	47.358	0.059	324
			2	6	1	47.379	0.038	60
			5	3	1	47.625		31
			3	1	3	47.910		105
			4	5	0	48.056		11
			6	0	0	48.789		31
			2	3	3	48.945		34
3	VW	49.376	3	6	0	49.369	0.007	0
			6	1	0	49.488	-0.112	118
			5	1	2	49.696		25
3	W	49.878	5	4	0	49.958	-0.080	258
			3	2	3	50.005	-0.126	12
3	VW	50.581	4	5	1	50.615	-0.033	149
			1	4	3	51.117		2
3	VVW	51.284	1	7	0	51.183	0.101	26
			6	0	1	51.358	-0.074	33
			0	6	2	51.412	-0.128	0
			6	2	0	51.602		0
			5	2	2	51.813		134
			3	5	2	51.926		6
			3	6	1	51.948		8
			4	4	2	52.010		89
			6	1	1	52.069	0.170	70
3	W(BR)	52.239	1	6	2	52.339	-0.100	296
			5	4	1	52.549		156
			0	7	1	52.861		55
			3	3	3	53.563		4
3	VW	53.780	4	0	3	53.649	0.130	2
			1	7	1	53.801	-0.022	230
			2	4	3	53.916	-0.137	2
			2	7	0	53.984		10
3	VW	54.244	6	2	1	54.231	0.013	196
			4	1	3	54.376	-0.132	83
3	W	55.198	2	6	2	55.174	0.025	151
			6	3	0	55.216	-0.018	69
			5	3	2	55.436		23
3	VW	55.877	4	6	0	55.919	-0.042	145
3	VW	56.605	5	5	0	56.460	0.145	38
			4	2	3	56.598	0.007	66
			2	7	1	56.687	-0.082	45
			0	5	3	56.718	-0.112	123
3	W	57.170	0	0	4	57.167	0.002	289
			1	5	3	57.632		0
			6	3	1	57.892		19
			4	5	2	58.599		11
			4	6	1	58.623		53
1	M	58.814	3	4	3	58.726	0.088	385
			3	7	0	58.798	0.016	43
			1	1	4	58.862	-0.048	11
			5	5	1	59.188		10
			6	0	2	59.422		37
			3	6	2	60.080		0
1	MW	60.233	0	2	4	60.202	0.031	3
			6	1	2	60.216	0.017	150
			4	3	3	60.400		13
			6	4	0	60.517		9
1	VW	60.786	2	5	3	60.698	0.088	49
			5	4	2	60.757	0.029	328
			2	0	4	61.181		0
			1	2	4	61.257		1
			0	8	0	61.417		57
			3	7	1	61.730		0
			2	1	4	62.006		1
			7	1	0	62.102		19
			1	7	2	62.186		33
			1	8	0	62.500		1
			6	2	2	62.683		0
1	W	63.498	5	1	3	63.499	-0.001	327
			6	4	1	63.566	-0.068	2
2	VW	63.875	5	1	3	63.787	0.087	164
			6	4	1	63.855	0.019	1
1	VW	64.691	2	2	4	64.586	0.105	70
			7	2	0	64.689	0.002	61
			7	1	1	65.280		0
			5	6	0	65.354		0
1	VW	65.544	1	3	4	65.573	-0.029	164
			2	7	2	65.601	-0.057	14
			1	8	1	65.714		17
1	VW	65.933	2	8	0	65.947	-0.013	86
1	VW	66.250	5	2	3	66.191	0.069	50
			3	5	3	66.339	-0.080	102
			4	4	3	66.451		13
			4	7	0	66.538		46
			1	6	3	66.888		115
			6	3	2	67.185		108
			3	1	4	67.875	0.155	280
1	M(BR)	68.030	4	6	2	68.115	-0.085	249
			7	2	1	68.132	-0.102	101
			6	5	0	68.545		4
			5	5	2	68.847		69
			5	6	1	68.879		1
			2	3	4	69.388		145
1	MW	69.549	7	3	0	69.509	0.040	113
			2	8	1	69.550	-0.001	309
2	VW	69.902	7	3	0	69.896	0.007	57
			2	8	1	69.938	-0.035	155
1	MW	70.302	4	7	1	70.225	0.077	426
2	VW	70.617	4	7	1	70.627	-0.010	213
			2	6	3	70.907		41
1	VW(BR)	71.082	3	2	4	71.027	0.055	223
			5	3	3	71.306		32
			0	4	4	71.340		39
			3	7	2	72.327		127
1	MW(BR)	72.562	6	5	1	72.568	-0.006	305
			3	8	0	72.779		0
			1	4	4	72.878		92
			7	3	1	73.730		27
			6	4	2	75.112		31
1	W	76.757	0	8	2	76.730	0.027	225
			4	5	3	76.923	-0.166	165
			3	3	4	77.690		66
			4	0	4	77.887		11
			3	8	1	77.948		13
			7	1	2	78.073		75
1	W	78.503	2	4	4	78.523	-0.020	39
			6	0	3	78.681		37
			7	4	0	78.729		74
			1	8	2	78.911		7
			4	1	4	79.698		59
			3	6	3	80.277		7
1	W	80.648	6	1	3	80.636	0.012	147
1	MW	82.169	5	4	3	82.208	-0.039	379
			6	1	3	81.549		73
2	MW	83.376	5	4	3	83.335	0.040	190

* Numbers given in first column: 3 = Cu $K\alpha$, 2 = Cu $K\alpha_2$, 1 = Cu $K\alpha_1$.

** THETA OBS is the observed value for the Bragg angle θ in degrees minus an absorption correction of the form

$$57{\cdot}29578 \, . \, K\lambda \, . \, (\cos\theta_r/\sin\theta_r + \cos\theta_r/\theta_r) \, . \, (1/4d),$$

in which θ_r is the Bragg angle in radians, d is the interplanar spacing, and K is an adjustable parameter (see text).

*** ICAL is the calculated powder intensity (without correction for absorption) divided by 100 and multiplied by 1, $\frac{1}{3}$, or $\frac{2}{3}$ in the respective cases α, α_2, α_1.

that all these *E*-silicides and germanides are characterized by a rather restricted range of homogeneity around the 1:1:1 composition.

Our studies based on tiny single-crystal fragments isolated from a crushed sample of TiNiSi(*E*), kindly sent to us by Professor Paul A. Beck (University of Illinois), did not confirm the large orthorhombic cell found by Spiegel *et al.* (1963). Approximate values for the cell dimensions were obtained from precession photographs and were refined by a least-squares fit of the lines observed on a powder diffraction diagram taken by the Straumanis method with Cu $K\alpha$ radiation in a Philips powder camera with 57·3 mm radius. A least-squares program LSCELP was written in FORTRAN for the IBM 7094 computer, similar to the ALGOL program described by Evans, Appleman & Handwerker (1963). An absorption parameter K was introduced in conjunction with the absorption function of Nelson & Riley (1945). An orthorhombic cell with the following cell dimensions was obtained for TiNiSi(*E*) on least-squares refinement:

$$a_0=6{\cdot}1484\pm0{\cdot}0012,\ b_0=7{\cdot}0173\pm0{\cdot}0014,$$
$$c_0=3{\cdot}6698\pm0{\cdot}0007\ \text{Å};\ K=(0{\cdot}92\pm0{\cdot}24)\times10^{-3}.$$

The limits given are standard deviations. Table 1 is the output of LSCELP and shows the indexing of the powder diagram and the agreement obtained for the observed and calculated theta values.

The systematic absences indicate that the space group is *Pnam* or *Pna*. The observed density (Spiegel *et al.*, 1963) is 5·66 $g.cm^{-3}$ and the calculated number of formula units per cell is 4·00. The ratios of the cell dimensions, the number of atoms per cell and the space group suggest that the structure of the *E* phase is related to the $PbCl_2$ structure (*C*23 type). Trial positional parameters were derived from the $PbCl_2$ structure, assuming Si in the Pb position and Ti and Ni in the two Cl positions so that Ti would have a larger number of neighbors than Ni. (In Ti- or Ni-containing Laves phases Ti occupies the CN16 position and Ni the CN12 position.) Intensities calculated for this structure were in reasonable agreement with the observed powder diffraction intensities.

Refinement of the structure

The structure was refined on the basis of structure amplitudes, obtained from the visual estimation of intensities recorded with Mo $K\alpha$ radiation by the equi-inclination Weissenberg method. Two irregular crystal flakes were used, one with largest dimension about 0·02 mm for the recording of layers (*hk*0)–(*hk*2) and one with largest dimension about 0·03 mm for layers (*h*0*l*)–(*h*2*l*). Although exposures up to 200 hours were used only 107 independent reflexions were strong enough to be observed.

The refinement was carried out by several cycles of full-matrix least-squares analysis on the IBM 7094 computer with the program ORFLS (Busing & Levy, 1962). The structure factors were calculated with the scattering factors tabulated in *International Tables for X-ray Crystallography* (1962). No absorption, extinction or dispersion corrections were applied. The standard errors in the structure amplitudes, on which the weights were based, were set equal to 4·0 for all reflexions with $|F_o|\le40$ and to $\frac{1}{10}|F_o|$ for $|F_o|>40$. Ten parameters were refined: an overall scale factor and for each atom an isotropic temperature factor and two positional parameters.

The refinement proceeded very rapidly from an initial R value of 0·399 to a final value of 0·086. The non-observed reflexions were excluded from refinement and from the R index; the 002 reflexion was also excluded from the last refinement cycle because of evidence of extinction. An analysis of R as a function of l did not show any trend inconsistent with confinement of all atoms to mirror planes as would be required by space group *Pnam* (D_{2h}^{16}). No structure factors calculated for the non-observed reflexions in the observed range of the reciprocal lattice exceed significantly the estimated values of $F_{\min}$, except for the reflexions 120 and 462, which were therefore included in the last refinement cycle. The R value including the non-observed reflexions with $|F_o|=\frac{1}{2}F_{\min}$ and including 002 is 0·191, the large increase probably resulting from the weakness of the photographs and the high values for $F_{\min}$.

In order to determine whether the three kinds of atom were placed correctly in the three positions one least-squares cycle was run in which only the positional parameters and the 'atom multipliers' (occupancy factors) were varied. This resulted in no significant changes in the parameters. The final parameters are given in Table 2 and the observed and calculated structure factors in Table 3.

Discussion

The interatomic distances listed in Table 4 were calculated with the IBM 7094 FORTRAN program DISTAN, written by one of us (D.P.S.). This program takes the coordinates of the atoms in the asymmetric unit, calculates the symmetry equivalent positions and searches all adjacent cells for distances below a specified limit.

Table 2. *Atomic parameters for* TiNiSi

Atom	CN	x	$\sigma(x)\,.\,10^4$	y	$\sigma(y)\,.\,10^4$	z	B	$\sigma(B)$
Ti	15	0·0212	10	0·1803	11	$\frac{1}{4}$	0·12	0·13
Ni	12	0·1420	8	0·5609	8	$\frac{1}{4}$	0·37	0·12
Si	9	0·7651	18	0·6229	18	$\frac{1}{4}$	0·24	0·19

Table 3. *Observed and calculated structure factors for* TiNiSi

H	K	FOBS	FCAL
	L=0		
2	0	*13	5
4	0	*19	9
6	0	38	34
8	0	48	49
1	1	31	30
2	1	15	-11
3	1	92	-95
4	1	29	25
5	1	22	-18
6	1	48	46
7	1	22	20
8	1	*25	4
0	2	26	24
1	2	** 8	-15
2	2	53	-52
3	2	71	-71
4	2	65	-67
5	2	41	41
6	2	*23	3
7	2	32	-33
1	3	69	77
2	3	64	-67
3	3	29	24
4	3	*28	9
5	3	*31	15
6	3	38	34
7	3	*38	40
0	4	37	-39
1	4	45	-48
2	4	*25	21
3	4	*27	-12
4	4	36	-32
5	4	65	68
6	4	*36	14
7	4	*39	23
1	5	51	-52
2	5	59	-65
3	5	*30	-8
4	5	*32	14
5	5	*34	-25
6	5	*37	8
0	6	*29	-3
1	6	55	-50
2	6	40	41
3	6	*32	-0
4	6	47	49
5	6	*37	1
6	6	*39	5
1	7	*33	-22
2	7	*34	-13
3	7	*35	31
4	7	*37	28
5	7	*39	14
0	8	49	-49
1	8	*36	-6
2	8	*37	-39
3	8	*38	-3
4	8	*40	23
	L=1		
2	0	84	93
4	0	*20	7
6	0	*25	-24
8	0	55	61
0	1	*10	1
1	1	38	33
2	1	84	-85
3	1	48	44
4	1	42	-38
5	1	72	-76
6	1	26	-25
7	1	*23	-0
1	2	81	88
2	2	50	45
3	2	21	-16
4	2	37	-32
5	2	29	25
6	2	48	-41
7	2	27	28
0	3	93	112
1	3	56	54
2	3	23	-24
3	3	*26	10
4	3	*29	-19
5	3	*32	17
6	3	*36	15
7	3	*39	12
1	4	*25	-5
2	4	*26	5
3	4	81	-91
4	4	*31	-13
5	4	42	-37
6	4	*37	5
7	4	*41	16
0	5	58	64
1	5	*28	0
2	5	39	29
3	5	39	-38
4	5	40	-36
5	5	*36	11
6	5	*39	43
1	6	41	40
2	6	*32	-23
3	6	*34	-8
4	6	40	25
5	6	*38	-3
6	6	*41	36
0	7	38	-31
1	7	47	-45
2	7	*35	-19
3	7	*37	-2
4	7	51	-54
5	7	*41	20
1	8	*38	12
2	8	51	-47
3	8	*40	7
	L=2		
0	0	E111	-165
2	0	*17	-3
4	0	*22	-8
6	0	33	-29
8	0	40	-44
1	1	24	-22
2	1	*15	9
3	1	69	75
4	1	25	-20
5	1	20	15
6	1	39	-41
7	1	24	-17
0	2	19	-19
1	2	*15	11
2	2	40	40
3	2	55	58
4	2	52	55
5	2	35	-34
6	2	*23	-2
7	2	35	30
1	3	54	-59
2	3	50	53
3	3	24	-20
4	3	*27	-7
5	3	*30	-14
6	3	39	-29
0	4	30	33
1	4	36	38
2	4	26	-18
3	4	*26	9
4	4	36	28
5	4	54	-60
6	4	*34	-12
1	5	43	43
2	5	48	54
3	5	*29	7
4	5	*31	-11
5	5	*33	22
6	5	*36	-7
0	6	*29	2
1	6	47	51
2	6	36	-36
3	6	*31	-0
4	6	**33	-44
5	6	*36	-0
1	7	*32	18
2	7	*33	11
3	7	*34	-28
4	7	*36	-25
0	8	47	44
1	8	*35	5
2	8	*36	35
	L=3		
2	0	51	-58
4	0	*26	-7
6	0	*30	16
8	0	51	-52
0	1	*18	-2
1	1	26	-19
2	1	54	55
3	1	35	-31
4	1	28	27
5	1	51	56
6	1	*24	21
1	2	53	-55
2	2	33	-29
3	2	*21	10
4	2	28	23
5	2	*24	-20
6	2	32	33
	L=4		
0	0	82	97
2	0	*27	1
4	0	*30	9
1	1	*22	12
2	1	*22	-4
3	1	46	-47
4	1	*24	14
5	1	*26	-11
6	1	33	31
0	2	*23	9
1	2	*23	-4
2	2	29	-25
3	2	37	-38
4	2	33	-37
	L=5		
2	0	35	34
0	1	*26	-1
1	1	*26	9
2	1	37	-36
3	1	*27	18
4	1	*28	-20
5	1	38	-38
	L=6		
0	0	56	-61

* Non-observed, value listed under FOBS is $F_{\min}$.
** Non-observed, but included in least-squares cycle.
E Left out of least cycle because of extinction.

Table 4. *Observed interatomic distances for* TiNiSi

The standard deviations in the distances average about 0·012 Å. The distances are given for the atoms listed in Table 2, going around each atom clockwise in Fig. 1(*a*) starting at 12 o'clock. Only distances smaller than 3·3 Å are listed.

	Ti		Ni		Si	
Towards atoms in the same plane	Si	2·603	Ti	2·881	Ni	2·358
	Ti	3·226	Si	2·344	Ni	2·344
	Ni	2·772	Si	2·358	Ti	2·603
	Ti	3·226	Ti	2·772		
	Ni	2·881				
Towards atoms in neighboring planes	Ti	3·136	Si	2·314	Ni	2·314
	Ni	2·891	Ti	2·891	Ti	2·646
	Si	2·646	Ti	2·770	Ti	2·574
	Ni	2·770	Ni	2·673		
	Si	2·574				

Fig. 1(*a*) gives the projection of the structure down the *z* axis. All atoms are situated in the mirror planes at $z=\frac{1}{4}$ and $\frac{3}{4}$ perpendicular to the *z* axis. The Si atom has a total of 9 near neighbors: 6 atoms (4 Ti + 2 Ni) at the corners of a triangular right prism (prism axis parallel to *z*) and 3 more atoms (2 Ni + 1 Ti) outside the rectangular prism faces in the same mirror plane as the center atom. The shortest Si–Si distances are 3·554 Å. This type of 9-coordination for Si is very commonly found for the metalloid atom in silicides, borides, phosphides and carbides (Aronsson, 1960).

The Ni atom has a total of 12 near neighbors: 8 atoms (4 Ti + 2 Ni + 2 Si) at the corners of a quadrangular right prism (prism axis parallel to *z*) and 4 more atoms (2 Ti + 2 Si) outside the side prism faces in the same mirror plane as the center atom. The twelvefold coordination around the Ni atom can be derived from a body-centered cubic arrangement (CN14) by elongating the cube in the direction of the *z* axis, so that the two Ni–Ni distances along the *z* axis become 3·670 Å, which is too long to be considered as a bonding distance. By contrast, in the frequently occurring $CuAl_2$ structure (*C*16 type) the Cu is at the center of a square anti-prism, which leads to a contraction along the *z* axis and larger distances to the four atoms in the equatorial plane, thus resulting in an effective coordination number of 10 for the Cu atom.

The Ti atom has a total of 15 near neighbors: 10 atoms (2 Ti, 4 Ni and 4 Si) at the corners of a pentagonal right prism (prism axis parallel to *z*) and 5 more atoms (2 Ti, 2 Ni and 1 Si) outside the rectangular prism faces in the same mirror plane. Two more Ti atoms are on the *z* axis at a distance of 3·670 Å from the center atom, that is, 0·45 Å farther away than the Ti atoms in the equatorial plane. One more Si atom in the center plane is at a distance of 3·482 Å. In the well known icosahedral arrangement of atoms as found in Laves phases, *β*-W phases and phases related to the *σ* phase, 10 atoms form a five-sided antiprism, which allows a closer approach of the atoms on the *z* axis and moves the atoms in the equatorial plane outward, thus giving the center atom 12 near neighbors.

Several transition element intermetallic compounds containing Si, Ge, P, *etc.* have been assigned the (*anti-*) $PbCl_2$-type ($C23$) structure (for references see Jellinek, 1959). Inspection of the cell dimensions of these compounds shows that most of them have a/b values in the range 0·67–0·73, namely: Rh_2Ge, δ-Ni_2Si, Co_2Si, Ru_2Si, Ir_2Si (Bhan & Schubert, 1960), Rh_2Si, Rh_2Ta (Giessen, Ibach & Grant, 1964), Rh_2Sn, Pd_2Sn, Pd_2Al, Pd_2Ga, Pd_2In. However TiNiSi (*E*), Co_2P, and Ru_2P (Rundquist, 1960) have a/b values in the range 0·84–0·88, which is within that reported for several other compounds with the $PbCl_2$-type or *anti*-$PbCl_2$-type structure, for instance ThS_2 (Zachariasen, 1949*b*), $ThSe_2$(D'Eye, 1953), Ca_2Si, Ca_2Ge, CaH_2 (Bergsma & Loopstra, 1962), $SnCl_2$ (van den Berg, 1961), and $PbCl_2$ itself. The atomic parameters determined for representatives of these two groups are not very different but the smaller a/b value for the compounds in the first group causes the numbers of neighbors for the various atoms to be significantly different from those we have described for TiNiSi. (A comparison of the Co_2Si and Co_2P structures is given by Rundquist, 1960).

The coordination polyhedra for the atoms in these structures are very complicated and the atomic surroundings may be best compared by examining the

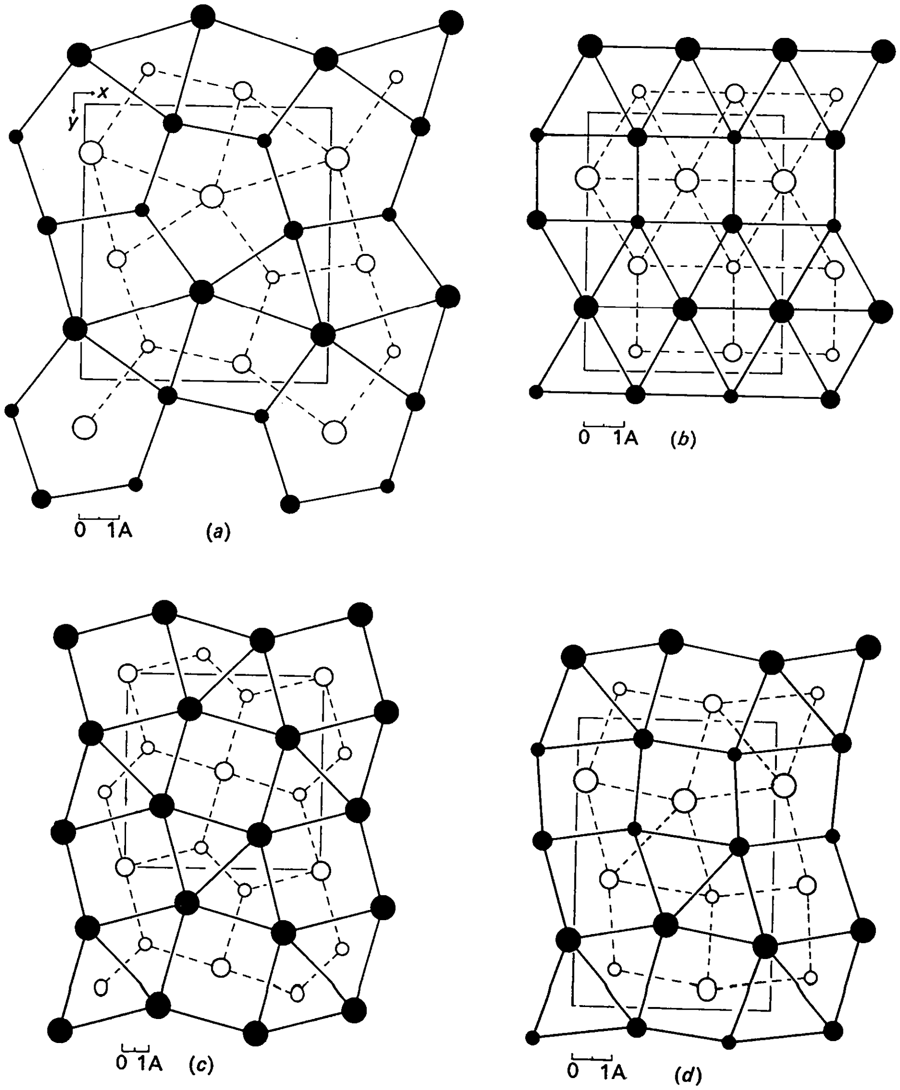

Fig .1 (*a*). Projection of TiNiSi down the z axis. Solid-line net at $-\frac{1}{4}$ (and$\frac{3}{4}$), broken-line net at $\frac{1}{4}$. (*b*) Projection of $\theta-Ni_2Si$ (Ni_2In type) down hexagonal [110]. Solid-line net at $-\frac{1}{4}$ (and $\frac{3}{4}$) and broken-line net at $\frac{1}{4}$ of [110] lattice repeat. (*c*) Projection of U_3Si_2 down the (tetragonal) z axis. Solid-line net at $z=\frac{1}{2}$, broken-line net at $z=0$. (*d*) Projection of Co_2Si down the z axis. Nets as in (*a*). The atoms are to be identified as follows:

	Large circles	Intermediate circles	Small circles
(*a*)	Ti	Ni	Si
(*b*)	Ni(I)	Ni(II)	Si
(*c*)	U(II)	U(I)	Si
(*d*)	Co(I)	Co(II)	Si

bonding networks lying in the mirror planes. The networks in Fig. 1 are drawn so that any distance between unconnected atoms is greater than the distance between any pair of connected atoms (Wells, 1954). Co_2Si, a representative of the first group, was first described by Geller (1955) as a distorted Ni_2In structure. A small distortion of the Ni_2In nets (which are drawn in Fig. 1(*b*) for θ-Ni_2Si; Toman, 1952) results in the Co_2Si structure with rather similar coordination polyhedra for the two transition metal atoms [Fig. 1(*d*)], but a much larger distortion is needed to accommodate the larger Ti atoms in the TiNiSi structure [Fig. 1(*a*)]. Going from the θ-Ni_2Si structure (Ni_2In type), through Co_2Si to the TiNiSi structure the numbers of near neighbors change as follows:

θ-Ni_2Si		Co_2Si		TiNiSi	
Ni(I)	14	Co(I)	13(+1?)	Ti	15(+3?)
Ni(II)	11	Co(II)	13	Ni	12
Si(In)	11	Si	10(+5?)	Si	9(+1?)

(The definition of 'neighbors' is, of course, to some degree arbitrary. The numbers in parentheses indicate the shading between neighbors and non-neighbors.)

The Co_2Si network is only a small distortion of the well known $3^2 . 4 . 3 . 4$ network which is shown by solid lines in the diagram of U_3Si_2 [Fig. 1(*c*); Zachariasen, 1949(*a*)] and which also occurs in the $CuAl_2$ structure type (Frank & Kasper, 1959) and as the secondary layer in the σ phase. The U_3Si_2 structure has two kinds of planar nets, in alternating sequence: the first one is the $3^2 . 4 . 3 . 4$ net already mentioned, which is formed by U(II) atoms, and the second one is a net consisting of pentagons formed by 3 Si and 2 U(I). The surroundings of the atoms in U_3Si_2 are very similar to those in TiNiSi which is built of two *identical* planar nets in different orientation, each consisting of triangles, quadrangles and pentagons. U(I) has surroundings similar to those of Ni with a practically nondistorted cube; U(II) corresponds to Ti and Si to Si.

The only other ternary compound described with the $PbCl_2$ structure is Pb(OH)Cl (Brasseur, 1940).

Professor P. A. Beck also kindly sent us a specimen of an alloy MnCoSi which we found to be indexable on an *E*-phase type cell with $a_0 = 5{\cdot}8543 \pm 0{\cdot}0016$, $b_0 = 6{\cdot}8526 \pm 0{\cdot}0017$, $c_0 = 3{\cdot}6853 \pm 0{\cdot}0013$ Å. The alloy presumably has the *E*-phase structure but no parameter refinement was carried out.

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