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The Crystal Structure of $Rh_{17}Ge_{22}$, an Example of a New Kind of Electron Compound.

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$Rh_{17}Ge_{22}$ crystallizes with a tetragonal unit cell of unusual dimensions with $a = 5{\cdot}604$, and $c = 78{\cdot}45$ Å. One unit cell contains 68 Rh and 88 Ge atoms which are arranged in a new kind of 'superstructure'. The superstructure has two different substructures of different cell dimensions, one being formed by the Rh atoms, the other by the Ge atoms.

A number of structurally related transition metal silicides, germanides and gallides are known having the same pair of substructures but with different relative dimensions. It is shown that the relative subcell dimensions are controlled by the available valence electrons. These electron compounds offer a unique case where the relative valence electron contribution of the transition elements can be determined simply by a measurement of the X-ray diffraction line positions. The obtained values can then be used to calculate the compositions of new transition metal compounds.

Introduction

In the system rhodium–germanium there exist four different compounds: Rh_2Ge, Rh_5Ge_3, RhGe and a germanium rich phase. The crystal structures of the first three have been determined by Geller (1955). Zhuravlev & Zhdanov (1956) determined the composition of the fourth germanide as Rh_3Ge_4 and they reported also a tetragonal unit cell with $a = 5{\cdot}7 \pm 0{\cdot}2$ and $c = 10{\cdot}0 \pm 0{\cdot}3$ Å. In connection with earlier studies on the structure of the transition metal disilicides (Nowotny, Kudielka & Parthé, 1956; Duffin, Parthé & Norton, 1964), we found it of interest to study the crystal structure of the remaining rhodium germanide, which we expected initially to be a digermanide.

Experimental

The rhodium germanide needed for this investigation could be prepared by different methods. One method was to melt mixtures of elementary Rh and Ge in graphite crucibles under a purified Ar atmosphere in an induction furnace. Compressed powder mixtures were also melted without crucibles in an arc melting furnace. These methods produced a well crystallized material from which it was not difficult to pick appropriate single crystals. Microcrystalline material for powder diffraction patterns was obtained from Rh and Ge powder mixtures sintered in evacuated quartz tubes at 700° for 4 weeks. To avoid a violent initial reaction between the starting materials, it was found useful to raise the temperature gradually to 700 °C over a week.

The presence of Ge lines in powder patterns of alloys composed as $RhGe_2$ indicated that the new phase was not a digermanide. X-ray and metallographic investigations of samples covering a range in Ge content showed that the true composition must be close to $RhGe_{1{\cdot}3}$ as suggested by Zhuravlev & Zhdanov (1956).

Powder and single-crystal diffraction techniques have been used for this structure study. For the determination of the crystal structure, intensities were recorded photographically with Mo $K\alpha$ radiation on a Nonius integrating Weissenberg camera using the multiple film technique and equi-inclination setting. To reduce the intensity of the diffracted beam we used copper foils of 0·001 inch thickness between the films. Very weak reflections were estimated from nonintegrated Weissenberg photographs taken with Mo $K\alpha$ and Co $K\alpha$ radiation.

The single crystal used for these photographs had the shape of a needle with a rectangular cross section ($0{\cdot}025 \times 0{\cdot}030 \times 0{\cdot}14$ mm). The crystal was rotated around the needle axes which proved to be the [110] axis. The intensities were estimated visually by using an intensity strip with spots scaled for 10% intensity difference. The scale factor between the integrated films was found to be on the average 3·02 between first and second film and 3·92 between second and third film. The difference in scale factors of 30% is apparently caused by the fluorescence of the copper foils. The middle film obtains fluorescent radiation from two adjacent copper foils and is darkened more relative to the first, and third film, in contact only with one copper foil. The intensities of all strong, medium and weak spots could be measured conveniently on integrated Weissenberg photographs and were corrected for Laue streaks; however, the pattern contained a considerable number of extremely weak reflections which could not be recorded on integrating Weissenberg photographs because of the increase in background for longer exposures. The intensities of those reflections – about 50% of the total – had to be measured on unintegrated Weissenberg photographs. To correct for spot extension and contraction the average of the intensities of the symmetry related spots was used (Kaane & Cole, 1949). The absorption correction was made on the assumption that the crystal has a cylindrical shape with $\mu R = 0{\cdot}5$ (Table 5.3.5 B in *International Tables for X-ray Crystallography*, Vol. II). To reduce the errors in the absorption correction due to deviation of the actual crystal shape from a cylinder, which could have amounted to 20%, all symmetry related reflections were measured and compared and an average intensity value was obtained. The zero and three upper level photographs were evaluated and intensities of 435 independent reflections were collected and used for the refinement.

Determination of the unit cell

The strong lines of the powder pattern of the rhodium germanide could be indexed with a tetragonal cell with $a = 5{\cdot}604 \pm 0{\cdot}002$ Å and $c = 4{\cdot}615 \pm 0{\cdot}003$ Å. However, a number of reflections remained which could not be indexed with this cell. By using precession photographs, it was found that the rhodium germanide has tetragonal symmetry with the above given translation period of 5·604 Å in its base plane. Other precession photographs containing the *hkl* reflections showed an arrangement of diffraction spots in which each of the strong spots fitted one or the other of two different reciprocal lattices which had the same tetragonal *a* axis but no simple common relationship in their *c* translation ($c_{\rm I} = 4{\cdot}61$, $c_{\rm II} = 3{\cdot}56$ Å). Considering all the weaker diffraction spots on the Weissenberg and precession photographs one had to assume a very long *c* axis. In principle it is possible to determine the true length of the *c* axis from the position of the diffraction spots on the Weissenberg or precession photographs. However, for very long translation periods and short distances on the film such measurements are inaccurate. We relied therefore on the very accurately measured θ values from Guinier powder photographs and on the fact that the true *c* axis must be a multiple of the above reported translation periods $c_{\rm I}$ and $c_{\rm II}$. A redetermination of these subtranslation periods using powder data gave $c_{\rm I} = 4{\cdot}615$ and $c_{\rm II} = 3{\cdot}566$ Å. The true *c* axis was found to be 17 times $c_{\rm I}$ or 22 times $c_{\rm II}$. The final unit-cell data of the tetragonal rhodium germanide are thus:

$$a = 5{\cdot}604 \pm 0{\cdot}002, \ c = 78{\cdot}45 \pm 0{\cdot}04 \text{ Å} .$$

With these data it was possible to index uniquely every diffraction spot on the single-crystal and powder photographs.

Owing to the unusually large value of the *c* axis and the considerable number of unobserved reflections we considered the possibility of twinning. However, a study of polished and etched (concentrated nitric acid) specimens under the metal microscope with polarized light gave no indication of polysynthetic twins.

Determination of the crystal structure

It has been mentioned that most of the strong lines of the powder pattern could be indexed with a tetragonal unit cell with $a = 5.604$ and $c_{\rm I} = 4{\cdot}615$ Å which is a subcell of the true cell. If one considers only those strong reflections which correspond to this subcell and determines the conditions for possible reflections one finds: *hkl* only with $h+k+l=2n$, *hk*0 only with $h=2n$ and *hhl* only with $2h+l=4n$. The only possible space group for the subcell is $I4_1/amd$ (D_{4h}^{19}), which has two equivalent fourfold, three eightfold and other more-fold point positions. From the experimental density of 9·0 g.cm^{-3} and the size of the subcell one can conclude that this cell contains on the average four formula units $RhGe_{1{\cdot}3}$, that is four Rh atoms and 5·2 Ge atoms. Assuming that the subcell is caused by the arrangement of the Rh atoms only one can place the 4 Rh atoms in equipoint 4(*a*): $000, 0\,\frac{1}{2}\,\frac{1}{4}$; $+[000, \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$, which corresponds to the atom arrangement in the white tin (*A*5) structure type. There are no other possibilities except 4(*b*), which gives an identical arrangement. An intensity calculation was made for the subcell, assuming only the presence of these 4 Rh atoms. Except for reflections with very high *l* values the intensities calculated for the subcell agreed well for all subcell reflections. This successful interpretation of the subcell was a decisive step for the solution of the crystal structure. From the size of the big unit cell it could be already concluded that there are 68 (17 times 4) Rh atoms in the unit cell. For the positioning of the Rh atoms in the long cell we were guided by the prominence of the subcell diffraction line and made the assumption that Rh subcells are stacked one on top of the other without any change in x or y, seventeen altogether in one unit cell.

Using the experimental density value one can calculate that the second, smaller subcell ($a = 5{\cdot}604$ Å and $c_{II} = 3{\cdot}566$ Å) must contain on the average 3·1 formula units $RhGe_{1{\cdot}3}$, that is four Ge atoms per subcell. Again we considered the reflections from the subcell and found from the systematic extinctions that the structure of this subcell must be face centered tetragonal. Assuming that the Ge atoms are responsible for the occurrence of these subcell reflections one can conclude that the four Ge atoms are centered in every subcell about positions: $000+[\frac{1}{2}\,\frac{1}{2}\,0\circlearrowright]$ or $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}+[\frac{1}{2}\,\frac{1}{2}\,0\circlearrowright]$. However, in contrast to the Rh subcell lines, the Ge subcell reflections rapidly lose intensity if the l value is large. Thus one can conclude that the Ge atom arrangement within the Ge subcell is face centered only to a first approximation. There are 22 Ge subcells in one long unit cell; therefore one unit cell of the rhodium germanide contains 68 Rh and 88 Ge atoms. The composition $Rh_{17}Ge_{22}$ expressed as a fraction is $RhGe_{1{\cdot}2941}$ which agrees well with the value $RhGe_{1{\cdot}3}$ obtained by metallographic examination.

Considering all of the observed diffraction lines of the long unit cell of $Rh_{17}Ge_{22}$ one can formulate the conditions for possible reflections as: hkl only with

Table 1. *Powder intensity calculation for* $Rh_{17}Ge_{22}$

Cr $K\alpha$ radiation

			Subcell indices				
h	k	l	Rh	Ge	$10^3 . \sin^2 \theta_c$	I_{cal}	I_{obs}
0	0	4			3·4	0·5	
0	0	8			13·6	0·2	
0	0	12			30·7	0·2	
1	0	1			42·0	0·1	
1	0	3			43·7	0·6	
1	0	5			47·1	0·0	
1	0	7			52·2	5·3	*vvvw*
0	0	16			54·6	0·2	
1	0	9			59·1	0·0	
1	0	11			67·6	0·1	
1	0	13			77·8	0·1	
1	1	2			84·4	0·4	
0	0	20			85·3	1·3	
1	0	15			89·8	0·1	
1	1	6			91·2	0·1	
1	0	17	101		103·4	101·6	*st*
1	1	10			104·9	15·2	
1	0	19			118·8	0·4	
0	0	24			122·9	0·4	
1	1	14			125·4	0·1	
1	0	21			135·8	0·0	
1	1	18			152·6	0·3	
1	0	23			154·6	0·3	
2	0	0	200	200	167·1	31·7	*m*
0	0	28			167·2	0·0	
2	0	2			168·0	0·1	
2	0	4			170·5	0·0	
2	0	6			174·8	0·0	
1	0	25			175·0	0·0	
2	0	8			180·8	0·1	
1	1	22		111	186·8	123·5	*st*
2	0	10			188·5	6·2	
1	0	27			197·2	3·9	
2	0	12			197·8	0·1	
2	0	14			208·9	0·0	
2	1	1			209·1	0·2	
2	1	3			210·8	0·3	
2	1	5			214·2	79·3	*mst*
0	0	32			218·3	0·0	
2	1	7			219·4	1·9	
1	0	29			221·0	0·0	
2	0	16			221·7	0·1	
2	1	9			226·2	0·3	
1	1	26			227·7	0·1	
2	1	11			234·7	0·1	
2	0	18			236·2	0·1	
2	1	13			244·9	0·4	
1	0	31			246·7	0·3	
2	0	20			252·4	0·4	
2	1	15			256·9	0·0	
2	0	22			270·3	0·1	
2	1	17	211		270·5	234·2	*vst*
1	0	33			274·0	0·0	
1	1	30			275·5	0·3	
0	0	36			276·3	0·0	
2	1	19			285·9	0·2	
2	0	24			289·9	6·9	*vvvw*
2	1	21			302·9	0·3	
1	0	35			303·0	0·1	
2	0	26			311·3	0·1	
2	1	23			321·7	0·1	
1	1	34	112		330·0	116·4	*st*
1	0	37			333·7	0·3	
2	2	0	220	220	334·3	82·6	*mst*
2	0	28			334·3	0·1	
2	2	4			337·7	0·0	
0	0	40			341·1	0·2	
2	1	25			342·2	0·8	
2	2	8			347·9	0·2	
2	0	30			359·0	0·1	
2	1	27			364·3	21·4	*w*
2	2	12			365·0	9·4	
1	0	39			366·1	0·1	
3	0	1			376·3	0·0	
3	0	3			378·0	0·1	
3	0	5			381·4	0·0	
2	0	32			385·5	0·0	
3	0	7			386·5	1·0	
2	1	29			388·2	1·5	
2	2	16			388·8	0·1	
1	1	38			391·4	0·2	
3	0	9			393·3	0·0	
1	0	41			400·2	4·7	
3	0	11			401·8	0·1	
3	0	13			412·0	0·0	
0	0	44		002	412·8	24·1	*w*
2	0	34			413·6	1·1	
2	1	31			413·8	0·0	
3	1	0			417·8	0·1	
3	1	2			418·7	0·2	
2	2	20			419·5	0·1	
3	1	4			421·2	0·3	
3	0	15			424·0	0·1	
3	1	6			425·5	0·2	
3	1	8			431·5	0·0	
1	0	43			436·0	0·2	
3	0	17	301		437·7	105·5	*st*
3	1	10			439·1	2·0	
2	1	33			441·1	0·1	
2	0	36			443·5	0·0	
3	1	12			448·5	6·8	*vvvw*

$h+k+l=2n$, $hk0$ only with $h=2n$ and hhl only with $2h+l=4n$. These conditions are the same as the ones for the Rh atom subcell which led to the unique space group $I4_1/amd$ (D_{4h}^{19}). The arrangement for the Rh atoms was already predetermined from the intensity considerations of the first subcell. It is possible to find such an atomic arrangement for the Rh atoms in this space group [equipoint 4(a) and eight times equipoint 8(e)]; however, there are no equipoints available to place the Ge atoms in the space left open by the Rh atoms. Thus, it had to be assumed that some of the supposed extinctions are not systematic extinctions; rather, the intensities of the particular reflections are very weak owing to the special nature of the structure. Tentatively we relaxed the extinction law which affected the least number of reflections: $hk0$ with $h=2n$ only. The possible space groups are then $I4_1md$ (C_{4v}^{11}) and $I\bar{4}2d$ (D_{2d}^{12}). Assuming the latter the Rh atoms were placed in 4(a) and eight times 8(c) with tentative z parameters: 4/68, 8/68, 12/68, 16/68, 20/68, 24/68, 28/68, 32/68. For the Ge atoms there remained as the only choice equipoint 8(d) and five times equipoint 16(e) with approximate z parameters: 1/88, 3/88, 5/88, 7/88, 9/88, 11/88. Thus always two Ge atoms occur at the same height. For the determination of the x and y parameters of 16(e) and the x parameter of 8(d) the question arose how these Ge pairs are stacked on top of the next, either parallel or crossed. It was shown above that one could conclude from the small Ge-atom subcell that the arrangement of the Ge atoms in the subcell is almost face centered; that means that the two Ge pairs of each subcell are in a crossed position. For the whole structure consisting of 22 Ge subcells stacked one on top of the next one could assume 44 Ge pairs each crossed with respect to their neighbors with approximate x and y values for 16(e) of $\pm\frac{1}{4}$. Geometrical considerations assuming a Rh radius of 1·34 Å and a Ge radius of 1·39 Å suggested that the Ge atom pairs are slightly rotated away from the ideal positions, resulting in a new set of x and y values for the Ge atoms. A preliminary intensity calculation with these data gave such good agreement with the observed powder data that it had to be concluded that the proposed structure was essentially correct. A powder intensity calculation using the refined parameters is given in Table 1. (The powder intensity computer program by Jeitschko & Parthé (1966) was used.) One notices that with few exceptions all the strong lines correspond to either the Rh or the Ge subcell. The respective subcell Miller indices are shown in the second and third columns.

Structure refinement

The structure was refined on an IBM 7040 computer using a full-matrix least-squares program originally written by Gantzel, Sparks & Trueblood (1961), later revised by Okaya. Owing to the large number of unobserved reflections the structure could be refined only if the unobserved reflections also were included in the least-squares program. The program was altered somewhat to allow the inclusion of unobserved reflections in the least-squares refinement in all instances where the calculated structure factors were stronger than the limit of observation. The function minimized was $\Sigma\,\omega^2(\Delta F)^2$ with $\omega=c/F_{\text{obs}}$; c was 1·0 for the more intense reflections (about 50% of the total observed) decreasing gradually to 0·5 for the unobserved reflections.

For the initial cycle, scale factors for the four layer lines were obtained by comparing observed and calculated F values of the strong reflections of the Rh subcell, which are relatively insensitive to shifts of the free parameters. Isotropic temperature factors were obtained by a graphical method described by Buerger (1960). Because of the special feature of the structure it is possible to obtain temperature factors for Rh and Ge atoms separately (there are enough reflections due almost entirely to one kind of atom).

A total of 25 parameters (24 positional parameters and one scale factor) were refined in the main cycles. After three subsequent main cycles, the program was used to refine a scale factor for each layer line separately (by fixing all positional parameters). At these stages the temperature factors were redetermined by

Table 2. *The final parameters of* $Rh_{17}Ge_{22}$ *and their standard deviations*

	x	y	z
Rh (1) in 8(c)	0	0	0·05761 (0·00008)
Rh (2) in 8(c)	0	0	0·11971 (0·00010)
Rh (3) in 8(c)	0	0	0·17446 (0·00011)
Rh (4) in 8(c)	0	0	0·23702 (0·00016)
Rh (5) in 8(c)	0	0	0·29322 (0·00010)
Rh (6) in 8(c)	0	0	0·35252 (0·00017)
Rh (7) in 8(c)	0	0	0·41361 (0·00008)
Rh (8) in 8(c)	0	0	0·46830 (0·00011)
Rh (9) in 4(a)	0	0	0
Ge (1) in 16(e)	0·3466 (0·0017)	0·2170 (0·0015)	0·01180 (0·00006)
Ge (2) in 16(e)	0·8462 (0·0018)	0·1934 (0·0017)	0·03147 (0·00007)
Ge (3) in 16(e)	0·3094 (0·0027)	0·3375 (0·0026)	0·05789 (0·00007)
Ge (4) in 16(e)	0·7279 (0·0015)	0·1451 (0·0017)	0·07835 (0·00006)
Ge (5) in 16(e)	0·1786 (0·0023)	0·3246 (0·0026)	0·10265 (0·00008)
Ge (6) in 8(d)	0·6475 (0·0025)	$\frac{1}{4}$	$\frac{1}{8}$

Table 3. *Calculated and observed structure factors of* Rh$_{17}$Ge$_{22}$

Reading from left to right, the columns contain the values *l*, 0·1$|F_{\text{cal}}|$, 0·1$|F_{\text{obs}}|$.

00l		
4	2	<4
8	3	<6
12	5	<8
16	7	<9
20	22	14
24	15	17
28	5	<12
32	5	<13
36	8	<14
40	18	<15
44	235	236
48	4	<16
52	15	<14
56	17	<15
60	18	<15
64	30	22
68	174	182
72	9	<15
76	3	<16
80	3	<16
84	18	<17
88	101	106
92	66	64
96	20	<21
100	16	<21
104	23	<22
108	20	<23
112	103	120
116	22	<24
120	2	<25
124	7	<26
128	15	<26
132	43	36
136	26	27
140	3	<27
144	12	<28
148	22	<28
152	14	<29
156	51	60
160	35	32
164	14	<29
168	9	<29
172	9	<29
176	20	<28
180	36	37
184	24	<28
188	10	<28
192	14	<27
196	6	<25
11l		
2	6	<6
6	4	<6
10	43	42
14	3	<7
18	8	<8
22	170	184
26	6	<9
30	10	<9
34	233	238
38	11	<10
42	25	18
46	33	38
50	1	<13
54	19	18
58	64	61
62	17	<14
66	92	97
70	4	<15
74	13	<15
78	88	93
82	28	18
86	23	17
90	35	42
94	4	<16
98	10	<17
102	64	67
106	17	<18
110	43	34
114	5	<19
118	10	<19
122	35	37
126	54	49
130	16	<21
134	26	31
138	4	<23
142	9	<24
146	49	56
150	27	<25
154	18	<25
158	7	<25
162	5	<25
166	15	<25
170	15	<25
174	12	<25
178	15	<24
182	1	<23
186	6	<22
190	26	23
22l		
0	281	312
4	1	<9
8	11	<9
12	69	82
16	6	<9
20	9	9
24	25	27
28	12	<10
32	43	43
36	1	<10
40	10	<11
44	99	110
48	15	<11
52	10	<11
56	58	70
60	4	<11
64	1	<12
68	129	135
72	10	<12
76	15	16
80	12	16
84	6	<15
88	42	40
92	61	55
96	10	<17
100	35	39
104	4	<19
108	6	<19
112	71	83
116	24	23
120	4	<21
124	14	<21
128	3	<22
132	20	<23
136	23	<23
140	8	<24
144	18	<24
148	5	<25
152	7	<25
156	33	33
160	32	28
164	8	<25
168	11	<24
172	3	<24
176	11	<23
180	30	27
184	22	<22
188	10	<21
192	4	<20
33l		
2	18	14
6	11	<11
10	83	93
14	3	<11
18	8	<11
22	23	31
26	5	<11
30	9	<11
34	237	267
38	6	<11
42	16	13
46	10	12
50	10	<12
54	43	39
58	43	41
62	14	<15
66	18	19
70	14	<16
74	4	<16
78	120	133
82	17	<18
86	12	<18
90	4	<19
94	7	<19
98	17	<20
102	71	84
106	6	<21
110	13	<21
114	14	<22
118	2	<22
122	56	61
126	46	42
130	15	<24
134	6	<24
138	1	<25
142	7	<25
146	58	67
150	25	<25
154	8	<25
158	7	<25
162	1	<25
166	25	<25
170	4	<24
174	6	<23
178	7	<22
182	4	<21
186	1	<20
190	32	32
44l		
0	113	117
4	2	<13
8	6	<13
12	57	71
16	12	<13
20	26	27
24	9	<13
28	12	<13
32	40	43
36	10	<15
40	10	<15
44	12	<16
48	13	<16
52	5	<16
56	53	64
60	15	<17
64	26	20
68	100	108
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132	13	<22
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140	9	<22
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146	9	<21
148	4	<21
150	2	<21
152	8	<21
154	7	<20
156	16	<20
158	5	<19
160	27	21
162	3	<19
164	7	<18
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4	4	<18
6	10	<18
8	9	<18
10	19	21
12	4	<18
14	12	<18
16	4	<18
18	1	<18
20	16	<18
22	10	<18
24	17	21
26	3	<19
28	6	<19
30	9	<19
32	2	<19
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36	11	<19
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44	10	<19
46	20	24
48	6	<19
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52	6	<20
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132	7	<22
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138	2	<21
140	3	<21
142	2	<21
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146	33	27
148	2	<21
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77	3	<14
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81	5	<14
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121	7	<20
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141	0	<24
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145	5	<24
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175	9	<25
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97	11	<18
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63	6	<17
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75	35	29
77	3	<19
79	7	<19
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87	0	<19
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97	9	<20
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101	3	<20
103	13	<21
105	23	26
107	7	<21
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165	1	<24
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63l		
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3	8	<15
5	18	20
7	35	42
9	9	<15
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17	110	115
19	12	<15
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37	31	29
39	15	18
41	13	<16
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47	7	<16
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51	109	114
53	14	<17
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74l		
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125	6	<24
127	8	<24
129	31	26
131	4	<24
133	14	<24

Table 4. *Interatomic distances in the structure of* Rh$_{17}$Ge$_{22}$

All distances shorter than 3·5 Å are listed.

			Mean*			Mean*
Rh (1)	2 Ge (4)	2·37±0·02	2·47	2 Rh (5)	3·02±0·01	3·08
	2 Ge (2)	2·47±0·02		2 Rh (3)	3·14±0·01	
	2 Ge (3)	2·57±0·02				
Rh (2)	2 Ge (6)	2·46±0·01	2·50	2 Rh (2)	2·92±0·01	3·01
	2 Ge (5)	2·47±0·03		2 Rh (6)	3·11±0·01	
	2 Ge (5′)	2·58±0·03				
Rh (3)	2 Ge (3)	2·40±0·03	2·49	2 Rh (7)	2·93±0·01	3·04
	2 Ge (4)	2·52±0·02		2 Rh (1)	3·14±0·01	
	2 Ge (5)	2·55±0·02				
Rh (4)	2 Ge (2)	2·41±0·02	2·46	2 Rh (9)	2·98±0·01	3·07
	2 Ge (1)	2·45±0·02		2 Rh (8)	3·16±0·02	
	2 Ge (1′)	2·51±0·02				
Rh (5)	2 Ge (2)	2·41±0·02	2·58	2 Rh (8)	2·94±0·01	2·98
	2 Ge (3)	2·46±0·02		2 Rh (1)	3·02±0·01	
	2 Ge (1)	2·88±0·02				
	2 Ge (4)	3·14±0·02				
Rh (6)	2 Ge (6)	2·40±0·02	2·46	2 Rh (7)	3·07±0·02	3·09
	2 Ge (4)	2·43±0·02		2 Rh (2)	3·11±0·01	
	2 Ge (5)	2·56±0·02				
Rh (7)	2 Ge (5)	2·42±0·02	2·50	2 Rh (3)	2·93±0·01	3·00
	2 Ge (4)	2·45±0·02		2 Rh (6)	3·07±0·02	
	2 Ge (3)	2·64±0·02				
	2 Ge (6)	3·44±0·02				
Rh (8)	2 Ge (1)	2·39±0·02	2·49	2 Rh (5)	2·94±0·01	3·05
	2 Ge (3)	2·49±0·03		2 Rh (4)	3·16±0·02	
	2 Ge (2)	2·59±0·02				
Rh (9)	4 Ge (1)	2·47±0·02	2·59	4 Rh (4)	2·98±0·01	2·98
	4 Ge (2)	2·83±0·02				
			Average Rh–Ge distance 2·50$_4$			Average Rh–Rh distance 3·03$_3$
Ge (1)	1 Rh (8)	2·39±0·02		1 Ge (2)	2·97±0·03	
	1 Rh (4)	2·45±0·02		1 Ge (1)	2·98±0·03	
	1 Rh (9)	2·47±0·02		1 Ge (1′)	3·15±0·03	
	1 Rh (4′)	2·51±0·02		1 Ge (1″)	3·17±0·03	
	1 Rh (5)	2·88±0·02		1 Ge (2′)	3·20±0·03	
				1 Ge (2″)	3·20±0·03	
Ge (2)	1 Rh (4)	2·41±0·02		1 Ge (2)	2·77±0·03	
	1 Rh (5)	2·41±0·02		1 Ge (1)	2·97±0·03	
	1 Rh (1)	2·47±0·02		1 Ge (1′)	3·20±0·03	
	1 Rh (8)	2·59±0·02		1 Ge (1″)	3·20±0·03	
	1 Rh (9)	2·83±0·02		1 Ge (3)	3·42±0·03	
				1 Ge (3′)	3·46±0·03	
Ge (3)	1 Rh (3)	2·40±0·03		1 Ge (3)	2·81±0·04	
	1 Rh (5)	2·46±0·02		1 Ge (4)	3·04±0·04	
	1 Rh (8)	2·49±0·03		1 Ge (4′)	3·15±0·03	
	1 Rh (1)	2·57±0·02		1 Ge (4″)	3·32±0·03	
	1 Rh (7)	2·64±0·02		1 Ge (2)	3·42±0·03	
				1 Ge (2′)	3·46±0·03	
Ge (4)	1 Rh (1)	2·37±0·02		1 Ge (4)	3·03±0·03	
	1 Rh (6)	2·43±0·02		1 Ge (3)	3·04±0·04	
	1 Rh (7)	2·45±0·02		1 Ge (3′)	3·15±0·03	
	1 Rh (3)	2·52±0·02		1 Ge (5)	3·29±0·04	
	1 Rh (5)	3·14±0·02		1 Ge (3″)	3·32±0·03	
				1 Ge (5′)	3·32±0·04	
				1 Ge (4′)	3·46±0·03	

Table 4 (*cont.*)

Ge (5)	1 Rh (7)	$2\cdot42 \pm 0\cdot02$	1 Ge (5)	$2\cdot81 \pm 0\cdot04$
	1 Rh (2)	$2\cdot47 \pm 0\cdot03$	1 Ge (6)	$3\cdot12 \pm 0\cdot02$
	1 Rh (3)	$2\cdot55 \pm 0\cdot02$	1 Ge (6′)	$3\cdot19 \pm 0\cdot03$
	1 Rh (6)	$2\cdot56 \pm 0\cdot02$	1 Ge (4)	$3\cdot29 \pm 0\cdot04$
	1 Rh (2′)	$2\cdot58 \pm 0\cdot03$	1 Ge (4′)	$3\cdot32 \pm 0\cdot04$
			1 Ge (6″)	$3\cdot48 \pm 0\cdot03$
Ge (6)	2 Rh (6)	$2\cdot40 \pm 0\cdot02$	2 Ge (5)	$3\cdot12 \pm 0\cdot02$
	2 Rh (2)	$2\cdot46 \pm 0\cdot01$	2 Ge (5′)	$3\cdot19 \pm 0\cdot03$
	2 Rh (7)	$3\cdot44 \pm 0\cdot02$	2 Ge (6)	$3\cdot25 \pm 0\cdot02$
			2 Ge (5″)	$3\cdot48 \pm 0\cdot03$

* Arithmetic mean of distances to six nearest Ge or four nearest Rh atoms.

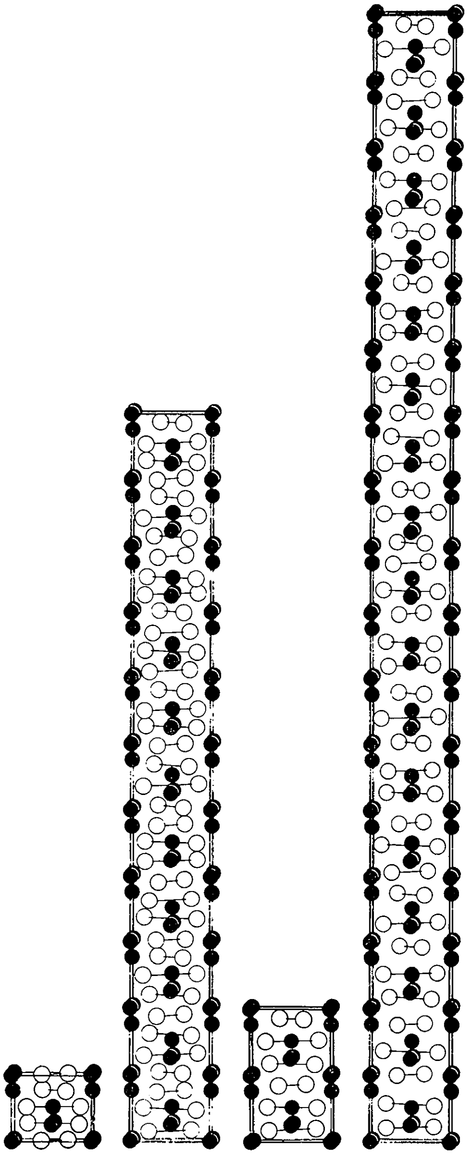

Fig. 1. A drawing of one unit cell each of four electron compounds: TiSi$_2$, Mn$_{11}$Si$_{19}$, Ru$_2$Sn$_3$ and Rh$_{17}$Ge$_{22}$. The subcell ratio c_T/c_M decreases from left to right and has the values 2·0, 1·727, 1·5 and 1·294.

the graphical method mentioned above. After that the next three main cycles were run. The procedure was repeated five times. It was felt physically more realistic to determine the temperature factors this way rather than to allow each atom a different temperature factor which may have no physical meaning at all. After the first 9 main cycles it could be seen that an anisotropic temperature factor for the Rh atoms could improve the agreement for those reflections *hkl* for which *l* is high. The refinement was considered to be final when the shifts of all parameters in the last three main cycles were less than the standard deviations computed from the inverse matrix. The final thermal factors are: Ge(isotropic) with $B=0\cdot5 \,.\, 10^{-16}$ cm^2 and Rh(anisotropic) with $B_a=0\cdot17$ 10^{-16} cm^2 and $B_c=0\cdot35 \,.\, 10^{-16}$ cm^2 where B_a and B_c are defined by the following expression for the effective atomic scattering factor:

$$f=f_o \,.\, \exp\left\{-\left[\frac{B_a}{4a^2}(h^2+k^2)+\frac{4c^2}{B_c}\,.\,l^2\right]\right\}$$

The values of the atomic scattering factors f_o were taken from *International Tables for X-ray Crystallography*, Vol. III, Table 3.3.1 B, p.210. The final positional parameters and their standard deviations are given in Table 2. The agreement between observed and calculated structure factors may be observed in Table 3. The final value of the discrepancy index, $R=\Sigma\,|F_{\rm obs}-|F_{\rm cal}||/F_{\rm obs}$, is 0·0912, excluding those reflections for which intensities were too weak to be measured.

Description of the new structure

One unit cell of Rh$_{17}$Ge$_{22}$ is shown on the right hand side of Fig. 1. The Rh atoms are indicated with filled circles and the Ge atoms with open circles. One easily recognizes the Rh subcells, stacked one on top of the next and consisting of four atoms each. Every Ge subcell contains two Ge dumb-bells which are alternately rotated in such a way that the atom arrangement in the subcell can be called, to a first approximation, face-centered tetragonal. However, in contrast to the rigid Rh subcell structures the Ge subcell structures differ slightly – one from the next – and may be also slightly rotated out of place.

The list of interatomic distances given in Table 4 reveals a strong interaction between Rh and Ge atoms.

Rh–Ge distances as short as 2·37 ± 0·02 and 2·39 ± 0·02 Å were found. Such short Rh–Ge distances have already been observed by Geller (1955) in Rh_5Ge_3 with Rh–Ge = 2·41 Å, and in this compound the coordination numbers were higher than they are for $Rh_{17}Ge_{22}$. Geller also found a systematic decrease and increase respectively in the average distances Rh–Ge and Rh–Rh for the compounds Rh_2Ge–Rh_5Ge_3–RhGe. If one compares the average of the distances of the six closest Ge atoms surrounding an Rh atom and the four relatively close Rh atoms which surround an Rh atom as listed in Table 5 one finds a consistent coherency for the compound $Rh_{17}Ge_{22}$ as the Ge-richest compound of the system Rh–Ge.

Table 5. *Average interatomic distances in* Rh–Ge *compounds*

Compound	Rh–Rh	Rh–Ge
Rh_2Ge	2·82 Å	2·57 Å
Rh_5Ge_3	2·84	2·54
RhGe	2·92	2·52
$Rh_{17}Ge_{22}$	3·03	2·50

The structural principle of $Rh_{17}Ge_{22}$ and related electron compounds

The term electron compounds is generally applied to intermetallic compounds which show a correlation between their stability range and the number or concentration of the participating electrons. Historically the well-known Hume-Rothery phases are the first known electron compounds where a certain value of the valence electron concentration has been connected with the occurrence of a particular structure type. Many other electron compounds have been found since. Some of the best studied examples are the transition metal disilicides (Nowotny, 1963) or the β-Mn, α-Mn, σ and related complex phases (Bardos, Malik, Spiegel & Beck, 1966) or the compounds with Cu_3Au stacking variations (Schubert, 1964). Finally, it has been shown that the concept of the valence electron concentration can be extended to nonmetallic compounds as demonstrated in the case of tetrahedral structure compounds (Parthé, 1963, 1964).

The compound $Rh_{17}Ge_{22}$ together with the silicides, germanides, stannides, aluminides and gallides listed in Table 6 and Fig. 2 are examples of a new kind of electron compound which can be derived from the $TiSi_2$ structure and show a unique mechanism for varying the composition and the number of the valence electrons. As can be seen from the position of the plots in Fig. 2 one may distinguish three series of electron compounds. One is the isostructural series with $TiSi_2$ (*C*54) structure type which extends horizontally across from $TiSi_2$ to $RuAl_2$, containing also aluminosilicides and gallogermanides. The other two series are non-isostructural. The first of these is the series from $TiSi_2$ to $Rh_{17}Ge_{22}$ marked by filled circles, containing only compounds with 4B elements, that are silicides, germanides or stannides and the second is the series from $RuAl_2$ to $Rh_{10}Ga_{17}$ marked by open circles, containing only compounds with 3B elements, that are aluminides and gallides.

First we will discuss the horizontal series (Fig. 2) of nine compounds all having the $TiSi_2$ structure type

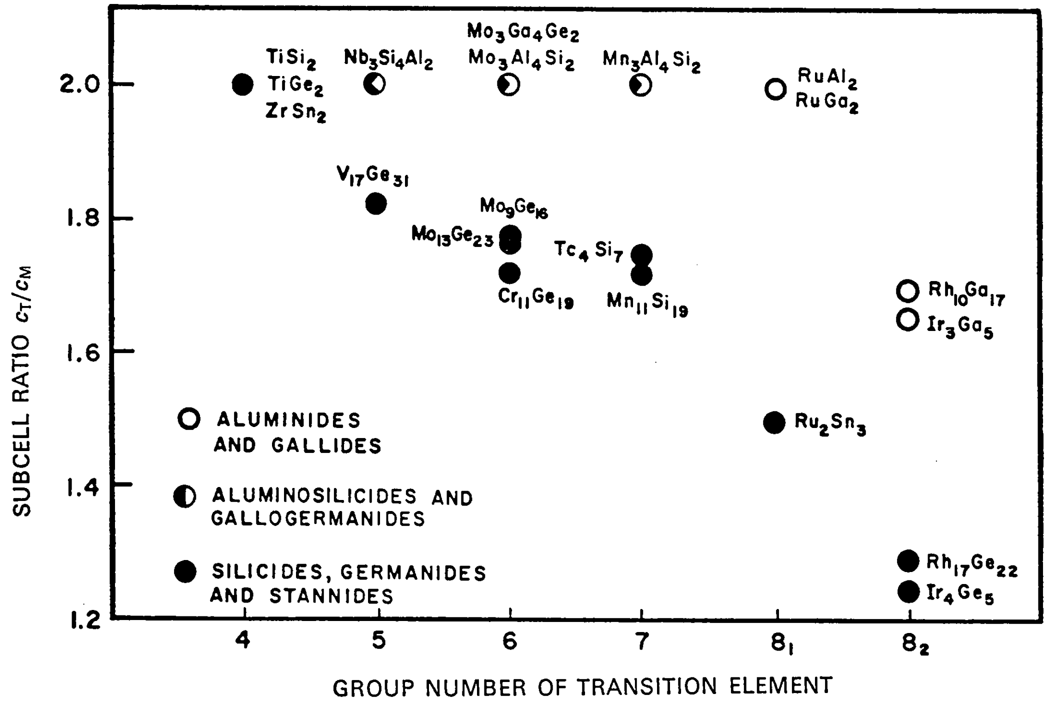

Fig. 2. The subcell ratio c_T/c_M and the composition of compounds TM_x (where $x = c_T/c_M$) as function of the group number of the T element.

Table 6. *Structure data of the related electron compounds with a white tin structure arrangement of the ıransition elements*

c_T/c_M	Compound	Valence electrons per T atom site	Structure type	Space group	a (Å)	c (Å)	Number of T subcells	c_T (Å)	Number of M subcells	c_M (Å)	Reference
	$TiSi_2$	12·000	$TiSi_2$		(5·83/6·04)*	4·783†	1	4·783	2	2·391	1
	$TiGe_2$	12·000	$TiSi_2$		(6·08/6·27)*	5·030†	1	5·030	2	2·515	2
	$ZrSn_2$	12·000	$TiSi_2$		(6·77/7·02)*	5·644†	1	5·644	2	2·822	3
	$Nb_3Si_4Al_2$‡	12·333	$TiSi_2$		(5·94/6·22)*	4·90$_1$†	1	4·90$_1$	2	2·45$_0$	4
	$Mo_3Al_4Si_2$‡	12·667	$TiSi_2$		(5·84/6·21)*	4·79$_3$†	1	4·79$_3$	2	2·39$_6$	5
2·000	$Mo_3Ga_4Ge_2$‡	12·667	$TiSi_2$	*Fddd* (D_{2h}^{24})	(5·95/6·23)*	4·92$_3$†	1	4·92	2	2·46	17
	$Mn_3Al_4Si_2$‡	13·667	$TiSi_2$		(5·54/6·02)* (5·58/6·01)*	4·53$_1$† 4·57$_0$†	1	4·53$_1$ 4·57$_0$	2	2·26$_5$ 2·28$_5$	6 15
	$RuAl_2$	14·000	$TiSi_2$		(5·67/6·21)*	4·71$_5$†	1	4·71$_5$	2	2·35$_7$	7
	$RuGa_2$	14·000	$TiSi_2$		(5·79/6·15)*	4·749†	1	4·749	2	2·374	8
1·823$_5$	$V_{17}Ge_{31}$	12·294	$V_{17}Ge_{31}$	$P\bar{4}n2$ (D_{2d}^8)	5·91	83·65	17	4·92	31	2·70	9, 16
1·777$_8$	Mo_9Ge_{16}	13·111	Mo_9Ge_{16}	$I\bar{4}2d$ (D_{2d}^{12})	5·994	43·995	9	4·88$_8$	16	2·74$_9$	14, 16
1·769$_2$	$Mo_{13}Ge_{23}$	13·077	$Mo_{13}Ge_{23}$	$P\bar{4}n2$ (D_{2d}^8)	5·99	63·54	13	4·88$_8$	23	2·76$_3$	9
1·750	Tc_4Si_7	14·000	Tc_4Si_7	$P\bar{4}c2$ (D_{2d}^6)	5·73$_7$	18·09$_9$	4	4·52$_5$	7	2·58$_6$	10
1·733	$Mn_{15}Si_{26}$	13·933	$Mn_{15}Si_{26}$	$I\bar{4}2d$ (D_{2d}^{12})	5·539	65·837	15	4·38$_9$	26	2·53$_2$	19
1·727$_3$	$Cr_{11}Ge_{19}$	12·909	$Mn_{11}Si_{19}$	$P\bar{4}n2$ (D_{2d}^8)	5·80	52·34	11	4·75$_8$	19	2·75$_5$	9
	$Mn_{11}Si_{19}$	13·909	$Mn_{11}Si_{19}$		5·518	48·136	11	4·37$_5$	19	2·53$_3$	11
1·700	$Rh_{10}Ga_{17}$	14·100	$Rh_{10}Ga_{17}$	$P\bar{4}c2$ (D_{2d}^6)	5·81$_3$	47·4$_6$	10	4·74$_6$	17	2·79$_2$	17
1·666$_7$	Ir_3Ga_5	14·000	Ir_3Ga_5	$P\bar{4}n2$ (D_{2d}^8)	5·82$_3$	14·20	3	4·73	5	2·84	17
1·500	Ru_2Sn_3	14·000	Ru_2Sn_3	$P\bar{4}c2$ (D_{2d}^6)	6·17$_2$	9·915	2	4·95$_7$	3	3·30$_5$	12
1·294$_1$	$Rh_{17}Ge_{22}$	14·176	$Rh_{17}Ge_{22}$	$I\bar{4}2d$ (D_{2d}^{12})	5·60$_4$	78·45	17	4·61$_5$	22	3·56$_6$	13
1·250	Ir_4Ge_5	14·000	Ir_4Ge_5	$P\bar{4}c2$ (D_{2d}^6)	5·64	18·24	4	4·56	5	3·64$_8$	18

* $TiSi_2$ (*C*54) type has an orthorhombic unit cell. Data given are the orthorhombic *a* and *c* values divided by $\sqrt{2}$.
† *b* axis of orthorhombic unit cell.
‡ In the original papers the compositions are given as $NbSi_{1.4}Al_{0.6}$, $MoAl_{1.3}Si_{0.7}$, $MoGa_{1.4}Ge_{0.6}$ and $MnAl_{1.3}Si_{0.7}$.

1. Laves & Wallbaum (1939).
2. Wallbaum (1944).
3. Nowotny & Schachner (1953).
4. Nowotny, Benesovsky & Brukl (1961).
5. Brukl, Nowotny, Schob & Benesovsky (1961).
6. Schubert, Meissner, Raman & Rossteutscher (1964).
7. Schwomma, Nowotny & Wittmann (1963).
8. Jeitschko, Holleck, Nowotny & Benesovsky (1963).
9. Voellenkle, Wittmann & Nowotny (1964).
10. Wittmann & Nowotny (1965).
11. Schwomma, Preisinger, Nowotny & Wittmann (1964).
12. Schwomma, Nowotny & Wittmann (1964).
13. This work.
14. Brown (1965).
15. Kuzma & Nowotny (1964).
16. Voellenkle, Preisinger, Nowotny & Wittmann (1966).
17. Voellenkle, Wittmann & Nowotny (1966).
18. Bhan & Schubert (1960).
19. Knott, Mueller & Heaton(1967).

These compounds are clearly electron compounds. It is not possible to state exactly the electron contribution of transition elements; however, it is obvious that Ti contributes less than Nb, Nb less than Mo and so on. In first approximation one can use the group number of the transition element as an indication of the valence electron contribution. Si or Ge with Ti, or Sn with its four electrons with Zr, can form the *C*54 structure. However, with Nb some of the Si atoms have to be replaced with Al atoms having only three electrons. For Mo more of the Si or Ge atoms have to be replaced with Al or Ga atoms, while in the case of Ru no Si atoms can be used. The *C*54 type occurs here with the dialuminide or the isoelectronic digallide. The series is a good example of a sequence of electron compounds having the same overall stoichiometry TB_2 except for the lack of composition change of the aluminosilicide between the Mo and the Mn compound.

The second and third series in Fig. 2 present a new kind of electron compound sequence which has varying stoichiometry. Structure drawings of four compounds belonging to the second series: $TiSi_2$, $Mn_{11}Si_{19}$, Ru_2Sn_3 and $Rh_{17}Ge_{22}$, are shown in Fig. 1. Schematic drawings of the different subcells for $V_{17}Ge_{31}$, $Cr_{11}Si_{19}$, Ru_2Sn_3 and $Rh_{17}Ge_{22}$ are presented in Fig. 3. Each of these structures consists of identical tetragonal transition metal subcells composed of four black T atoms. In $TiSi_2$ there is only one such subcell, in one unit cell of $Mn_{11}Si_{19}$ there are eleven stacked one on top of the other, in Ru_2Sn_3 two and in $Rh_{17}Ge_{22}$ seventeen. The number of subcells stacked in one unit cell is listed in Table 6 under the heading *Number of T subcells*, and their height under c_T(Å). All these subcells are tetragonal except for the compounds with *C*54 structure type which actually have orthorhombic symmetry, but for the sake of systematics one may consider them pseudo-tetragonal.* In the $TiSi_2$ unit cell shown in Fig. 1 there are eight Si atoms, arranged in two (to a first approximation) face centered subcells stacked one on top of the other, each containing four M(=Si, Ge or Sn) atoms. All the other structures shown in Fig. 1 or listed in Table 6 contain such M subcells; however, they are now more widely spaced and the M atoms may be slightly rotated from their ideal positions to avoid overlap with the atoms from the rather rigid transition metal partial structure.† The number of M subcells within one unit cell is given in Table 6 under the heading *Number of M subcells* and their individual height in the following column.

The parameter of interest for the discussion of these compounds is the subcell ratio c_T/c_M listed in the first column of Table 6. The ratio is directly correlated with the composition of the compounds according to TM_{c_T/c_M}. Actually, as the T and M subcell dimensions can be obtained with great accuracy from the powder diagram, it is possible to determine the compositions of the compounds much more accurately from X-ray diffraction data than by chemical analysis. As can be seen in Fig. 2, the subcell ratio c_T/c_M varies with the group number of the transition element. For example, in the series of the germanides it decreases steadily from 2·0 for $TiGe_2$ to 1·294 for $Rh_{17}Ge_{22}$. The subcell ratios differ also depending on whether the M component is a 4B or a 3B element. The data points in Fig. 2 lie roughly in two sloped bands, one containing 4B compounds (completely filled circles) and another – vertically displaced – 3B compounds (completely open circles).

It seems that the change in composition and subcell ratio with a change in group number of the transition metal component, and the band shift in Fig. 2 between 4B and 3B compounds, can be explained in a simple manner. We may assume that the actual structure-determining framework is the atomic arrangement of the transition metal atoms with the remaining atoms positioned in the available holes of the rigid T framework. To build this framework the T elements need additional electrons which are supplied by the B elements. As 4B elements can supply more electrons than the 3B elements, in comparison with 3B compounds the 4B compounds will contain less of the M component, and this explains the shift in the bands between 4B and 3B compounds in Fig. 2. It is interesting to note that one can calculate the corresponding compositions of 3B and 4B compounds and that correct results are obtained if one assumes that all the outer valence electrons of the B elements are placed at the disposal of the transition metal framework. If $T_1M_x^{3B}$ and $T_1M_y^{4B}$ are the corresponding compositions of the 3B and 4B electron compounds the simple relation is $3x=4y$; some results and examples are given in Table 7.

The change in composition and subcell ratio as a function of the group number of the transition metal

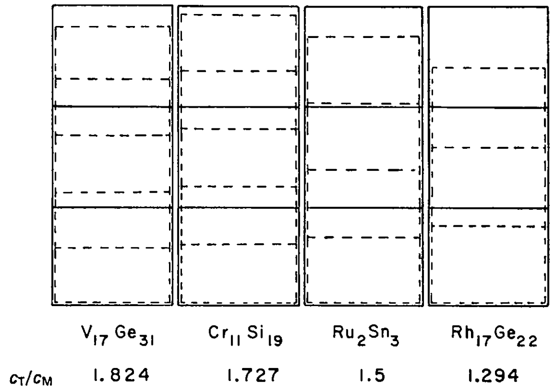

Fig. 3. Schematic drawing of the T and M subcells for $V_{17}Ge_{31}$, $Cr_{11}Si_{19}$, Ru_2Sn_3 and $Rh_{17}Ge_{22}$. T cell: solid lines, M cell: broken lines.

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* The crystal structure of $TiSi_2$ (*C*54 type) is based on a face centered orthorhombic Bravais lattice. However, if *a* and *c* values of $TiSi_2$ are tentatively assumed to have equal length, the structure can be considered as being face centered tetragonal. The corresponding smaller body centered tetragonal unit cell is shown at the left of Fig. 1.

† The dimensions of the M subcell can be easily calculated from the 111 and 002 M-subcell reflections which are observed to be strong in all diffraction patterns.

component within the band of 4B compounds and also within the band of 3B compounds can be traced to the different numbers of electrons the different transition elements bring with themselves. If the transition metal itself has more electrons, less of the electron donor is needed and consequently the compound will contain less Si, Ge, Sn, Al or Ga, the M subcell will be spaced wider, and the subcell ratio will be smaller. Irregularities occur with the Mn and Tc compounds. The deviations coincide with the deviations discussed above for the isostructural series with *C*54 type. In the case of molybdenum germanides two phases occur: $Mo_{13}Ge_{23}$ and Mo_9Ge_{16}, both having quite different tetragonal *c* axes, but rather similar subcell ratios.* Even very small changes in the electron demand of the transition metal may lead to big changes in the unit-cell dimensions as the translation period of the crystal must correspond to integral multiple units of T and M subcells. This demonstrates again that the important parameter for the discussion of these phases is the subcell ratio and not the actual size of the unit cells.

The above given interpretation of the electron compounds was that these compounds form if a certain number of electrons – provided together by the transition metal atoms and the 3B or 4B elements – is available for the construction of the rigid transition metal framework. We may test this assumption by calculating for each compound the total number of valence electrons per transition atom site. To obtain these values (given in the third column of Table 6) we inserted for the transition elements as a first approximation the total number of electrons outside the next lower inert gas configuration which is identical with the group number of the transition elements, except for Rh and Ir which were assumed to have 9 electrons each. Elements of the 4B and 3B groups were assumed to contribute 4 and 3 electrons respectively. If our assumption that these compounds occur only with a particular electron concentration on the transition atom sites is correct, all the electron compounds should have the same values for valence electrons per T atom site.

The experimental data are plotted in Fig. 4 against the group number of the transition metal component. Instead of the expected horizontal line, one finds that the data plots are spread along a sloped line which increases from 12 for Ti and Zr compounds to about 14 for compounds of the Fe group. To Fig. 4 have been added plots for some new compounds recently reported by Voellenkle, Wittmann & Nowotny (1966). The new Ru, Rh and Ir compounds are all electron compounds of the $TiSi_2$ structure family with valence electron/T atom site ratios close to fourteen. To avoid overcrowding of the diagram not all reported compounds have been listed in Fig. 4. One notices that in some cases different compounds of the same transition element have different values for valence electrons per T atom site, the biggest difference of 0·4 occurring between Mo_9Ge_{16} and $Mo_3Ga_4Ge_2$. However, it is perhaps not appropriate to compare the tetragonal phases with the orthorhombic phases having *C*54 structure. The orthorhombic distortion of the $TiSi_2$ type cannot be explained. It is quite possible that the electron requirement for the orthorhombic transition metal framework is different from the requirement for the tetragonal framework. Thus, we will restrict all our further considerations only to the truly tetragonal phases. The biggest difference in values for valence electrons per T atom site, considering only tetragonal phases containing the same transition element, is 0·2, which is a rather small value.

The question arises whether Fig. 4 cannot perhaps be used to determine the actual relative valence electron contributions of the transition elements in the tetragonal compounds. We have seen that in principle there exist no restrictions on the particular c_T/c_M values in these compounds. Slight changes in the valence electron contribution of the transition elements can easily be compensated by expanding or contracting the M subcell. Thus one wonders why the data in Fig. 4 do not fall on a horizontal line. The observed sloped line is obviously an indication that the approximation used above for the number of the transition metal valence electrons is not quite correct. The deviations of the values for valence electrons per T atom site in Fig. 4 from a horizontal line perhaps correspond to the deviations of the true electron contribution of the transition elements from the group number relation used for a first approximation. For example the group number difference between V and Rh is 4, assuming group number 9 for Rh. According to the rough approximation Rh in $Rh_{17}Ge_{22}$ should provide 4 electrons more for bonding than V in $V_{17}Ge_{31}$. However, the data points for these compounds in Fig. 4 show a valence electron per T atom site difference of 1·88. Therefore

Table 7. *The corresponding compositions of* 3B *and* 4B *electron compounds*

$T_1M_x{}^{3B}$		$T_1M_y{}^{4B}$	
Composition	Example	Composition	Example
TM_2	$RuGa_2$	T_2M_3	Ru_2Sn_3
T_3M_5	Ir_3Ga_5	T_4M_5	Ir_4Ge_5
$TM_{1\cdot725}$	($Rh_{10}Ga_{17}$) slight deviation from ideal value but very close.	$T_{17}M_{22}$	$Rh_{17}Ge_{22}$

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* The possibility of an electron change in Mo compounds was also recently demonstrated by Aubry, Duval & Roques (1965) who surprisingly found the *C*40 type for $MoSi_2$, while the *C*11 type is considered normal. These two types are known to be controlled by valence electron concentration.

Rh in $Rh_{17}Ge_{22}$ supplies only $4-1{\cdot}88=2{\cdot}12$ electrons more than V in $V_{17}Ge_{31}$.

The last result could also have been derived directly from the subcell ratios of the two compounds. The value for valence electrons per T atom site for $V_{17}Ge_{31}$ is

$$(17\times5+31\times4)/17=5+4\times(31/17)$$

or

$$5+4\times(c_T/c_M)_{V17Ge31}\,.$$

This value should be equal to

$$5+\Delta+4\times(c_T/c_M)_{Rh17Ge31}$$

where Δ is the difference in the true valence electron contribution of Rh in $Rh_{17}Ge_{22}$ from that of V in $V_{17}Ge_{31}$. Thus one obtains

$$\Delta=4\times[(c_T/c_M)_{V17Ge31}-(c_T/c_M)_{Rh17Ge22}],$$

or with actual numbers

$$\Delta=4\times(1{\cdot}823_5-1{\cdot}294_1)=2{\cdot}11_7.$$

The factor 4 in the equation above comes from our assumption that Ge contributes 4 electrons to the bonding scheme. This assumption appears to be valid as it allows us to calculate correctly the compositions of corresponding 4B and 3B compounds shown in Table 7. The factor has to be changed appropriately to 3 if gallides are to be compared with other gallides. It is evident that the true valence electron contribution of V in $V_{17}Ge_{31}$ does not need to be known for these calculations.

With the analytical expression above or data points from Fig. 4 the relative valence electron contributions of the transition elements in the tetragonal electron compounds listed in Table 6 have been calculated with the valence electron contribution of V in $V_{17}Ge_{31}$ as reference point. The results are shown in Table 8. The numbers listed are the numbers of electrons (or fractions thereof) a particular transition element in a particular compound provides to the bonding scheme in excess of all the electrons provided by V in $V_{17}Ge_{31}$. The data are presented graphically in Fig. 5. The valence electron contribution of the transition metal atoms increases very slowly up to the group 7 elements. Cr in $Cr_{11}Ge_{19}$ and Mn in $Mn_{11}Si_{19}$ actually provide the same number of valence electrons. Beyond group 7 the valence electron contribution increases by one electron for every group. This is clearly demonstrated in the series Tc_4Si_7, Ru_2Sn_3 and Ir_4Ge_5 with the relative

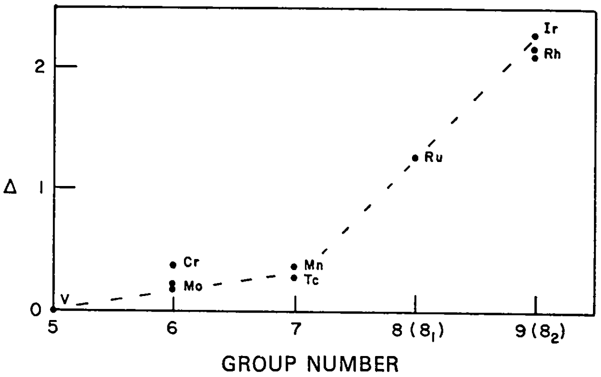

Fig. 5. The valence electron contribution of the transition elements in excess of the valence electron contribution of V in $V_{17}Ge_{31}$.

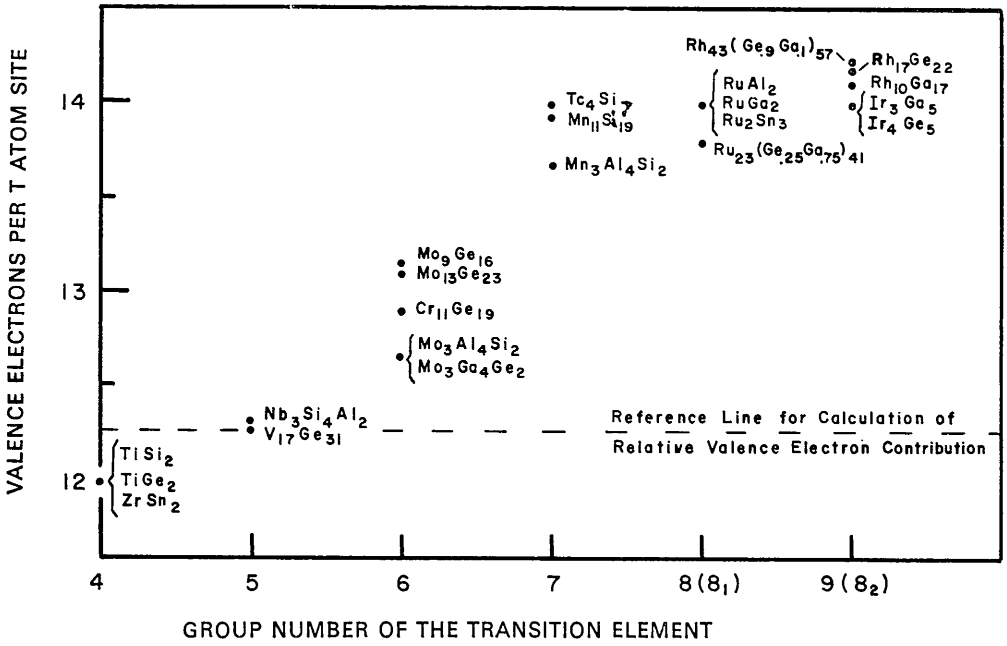

Fig. 4. The values of valence electrons per T atom site for the new electron compounds *versus* the group number of the transition metal component.

transition metal electron contributions of $0{\cdot}29_4$, $1{\cdot}29_4$ and $2{\cdot}29_4$. The relative valence electron contributions of the different transition metals in their different compounds fall within narrow limits on the dashed line in Fig. 5.

Table 8. *The relative valence electron contributions of the transition elements in reference to the contribution of* V *in* $V_{17}Ge_{31}$

Mo in Mo_9Ge_{16}	$0{\cdot}18_3$	Ru in Ru_2Sn_3	$1{\cdot}29_4$
Mo in $Mo_{13}Ge_{23}$	$0{\cdot}21_7$	Rh in $Rh_{17}Ge_{22}$	$2{\cdot}11_7$
Tc in Tc_4Si_7	$0{\cdot}29_4$	Rh in $Rh_{10}Ga_{17}$	$2{\cdot}19_4$
Mn in $Mn_{15}Si_{26}$	$0{\cdot}36_1$	Ir in Ir_4Ge_5	$2{\cdot}29_4$
Cr in $Cr_{11}Ge_{19}$	$0{\cdot}38_5$	Ir in Ir_3Ga_5	$2{\cdot}29_4$
Mn in $Mn_{11}Si_{19}$	$0{\cdot}38_5$		

An ideal case is presented by iridium, which always contributes exactly the same number of valence electrons. It is perhaps of interest to note that one can use this to calculate the compositions of new Ir compounds. For example, the relative valence electron contribution of Ir in Ir_4Ge_5 and Ir_3Ga_5 is $2{\cdot}29_4$ and the relative valence electron contribution of Rh in $Rh_{17}Ge_{22}$ is $2{\cdot}11_7$. If one intends to synthesize an iridium germanide with $Rh_{17}Ge_{22}$ structure a small percentage of the Ge atoms would have to be replaced with – let us assume – Ga atoms, which provide only 3 electrons each. We can actually calculate what the composition of the gallogermanide with $Rh_{17}Ge_{22}$ structure should be. If we write for its formula $Ir_{17}(Ge_{1-x}Ga_x)_{22}$ we can formulate mathematically the total valence electron concentration at the Ir atom sites as

$$(\text{Electron contribution})_{\text{V in V}_{17}\text{Ge}_{31}} + 2{\cdot}29_4 + (22/17) \times [4 \times (1-x) + 3x].$$

The value must be the same as the total valence electron concentration on the Rh sites in $Rh_{17}Ge_{22}$ which is given by

$$(\text{Electron contribution})_{\text{V in V}_{17}\text{Ge}_{31}} + 2{\cdot}11_7 + (22/17) \times 4.$$

The equation can be solved for x; the composition so found for an expected iridium gallogermanide with $Rh_{17}Ge_{22}$ structure is $Ir_{17}(Ge_{0{\cdot}863}Ga_{0{\cdot}137})_{22}$. Voellenkle, Wittmann & Nowotny (1966) have just reported that they found the $Rh_{17}Ge_{22}$ structure for an iridium gallogermanide of composition $Ir_{17}(Ge_{0{\cdot}85}Ga_{0{\cdot}15})_{22}$, in excellent agreement with the theoretical value.

The same paper gives the lattice constants and T metal subcell dimensions of three additional iridium gallogermanides which belong to the same group of electron compounds and have compositions between Ir_4Ge_5 and Ir_3Ga_5. Their ratio of T metal to M metal was determined very accurately from the X-ray data. We can use this information to calculate for each compound what the proper mixing ratio Ge:Ga should be. If the formula of the gallogermanide is written $Ir_T[Ge_{1-x}Ga_x]_M$, and if we assume that each Ir atom in all iridium gallogermanides always contributes the same number of valence electrons to the bonding scheme all iridium gallogermanides must have the same value of

$$(M/T)\,.\,[4\,(1-)x+3x],$$

which can easily be solved for x. Table 9 contains a list of the observed and the calculated iridium gallogermanide compositions. The agreement is very good except for a small deviation between observed and calculated composition for $Ir_2(Ge, Ga)_3$. However, according to Voellenkle, Wittmann & Nowotny (1966), this compound – although belonging to the electron compounds – has an irregular unit cell in which the tetragonal *a* axis is doubled. Therefore some details of the substructure in $Ir_2(Ge, Ga)_3$ must be different from the substructures of the other electron compounds, and thus we should not necessarily expect the valence electron rules to be applicable to $Ir_2(Ge, Ga)_3$ without any modification.

Table 9. *Observed and calculated composition of the series of electron compounds between* Ir_4Ge_5 *and* Ir_3Ga_5

Observed compositions	Calculated compositions
Ir_4Ge_5	Ir_4Ge_5
$Ir_{17}(Ge_{0.85}Ga_{0.15})_{22}$	$Ir_{17}(Ge_{0.863}Ga_{0.137})_{22}$
$Ir_{11}(Ge_{0.65}Ga_{0.35})_{15}$	$Ir_{11}(Ge_{0.666}Ga_{0.333})_{15}$
$Ir_2(Ge_{0.40}Ga_{0.60})_3$	$Ir_2(Ge_{0.333}Ga_{0.666})_3$
$Ir_{19}(Ge_{0.20}Ga_{0.80})_{30}$	$Ir_{19}(Ge_{0.166}Ga_{0.833})_{30}$
Ir_3Ga_5	Ir_3Ga_5

It was shown above that the new electron compounds present a unique case in which the relative valence electron contributions of the different transition elements can be determined very simply by measuring the positions of X-ray diffraction lines. It would be of extreme interest to know if these values can be substantiated by low temperature specific heat measurements or other physical experiments.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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Trioctahedral one-layer micas. III. Crystal structure of a synthetic fluormica. Errata.

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Corrections to *Acta Cryst.* **20**, 638 (1966),

The following corrections should be made in our paper on synthetic fluormica (Takeda & Donnay, 1966):

p. 641, col. 2, line 11 and p. 643, col. 1, line 20 up: instead of $1/2\sigma^2$, read $1/(2\sigma)^2$.

p. 641, Table 3(*a*), line 7: instead of −0·007, read −0·07.
p. 643, Table 8, lines 3 and 8: instead of υ, read ν.
p. 645, col. 2, lines 8 and 10: instead of γ, read ν.
p. 645, col. 2, line 13: instead of a, b, c^*, read $\mathbf{a}, \mathbf{b}, \mathbf{c}^*$.

Reference

Takeda, H. & Donnay, J. D. H. (1966). *Acta Cryst.* **20**, 638.

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