retical value $M_0 = 219$. The values $M_{t,\mathrm{obs}}$ and $M_{t,\mathrm{calc}}$ can then be compared, which was done with our new data. The conclusion of Mackay, that there should exist 41 more space groups than have actually been observed, could be confirmed to a certain extent, because the number of space groups without realization decreased from 41 to 22, as mentioned above.

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Rare earth–germanium and –silicon compounds at 5:4 and 5:3 compositions.

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Thirteen new rare earth germanides and eleven new rare earth silicides of 5:4 stoichiometry have been prepared. Lattice constants and structure-types have been determined, principally by single-crystal techniques. For the R_5Ge_4 compounds, all of the lanthanide elements studied show the orthorhombic 5:4 phase previously found for Sm_5Ge_4. (Rare earth metals not studied were Pm, Eu and Yb; in addition to these, Ho and Tm were not studied in the R_5Si_4 series.) The situation for the analogous silicon compounds is more complex. Tb_5Si_4, Dy_5Si_4, Er_5Si_4 and Y_5Si_4 crystallize with the Sm_5Ge_4-type structure; Sm and Gd probably do also, although no single crystals were obtained from these two preparations. La_5Si_4, Ce_5Si_4, Pr_5Si_4 and Nd_5Si_4 form tetragonal crystals, possibly of the Zr_5Si_4 type, whereas Lu_5Si_4 exhibits a monoclinic distortion of the orthorhombic phase. Ce_5Si_3 and Pr_5Si_3 were found to form tetragonal crystals of the Cr_5B_3 structure type. Powder-pattern data in the literature for La_5Si_3 could also be indexed on the basis of this structure type.

The recent characterization (Smith, Johnson & Tharp, 1967) of an orthorhombic phase in the samarium–germanium system as Sm_5Ge_4 has led to the present investigation of other rare earth–germanium and –silicon systems for the occurrence of this new structure type.

Rare earth–silicon compounds at the neighboring composition, R_5Si_3, were shown by Gladyshevskii & Kripyakevich (1964) to be of the $D8_8$ Mn_5Si_3 structure type for R = Gd through Lu. A subsequent investigation (Gladyshevskii, Dvorina, Kulikova & Verkhoglyadova, 1965) of the La–Si system indicated the formation of La_5Si_3, but its structure type was not specified. The present study shows Ce_5Si_3 and Pr_5Si_3 to have a structure of the $D8_l$ Cr_5B_3 type. An examination of the data for La_5Si_3 indicates a similar structure type for this compound.

Experimental

Samples were prepared by mixing appropriate quantities of metal with either germanium or silicon, and arc-melting the mixture in a gettered atmosphere of argon. To improve their homogeneity, the fused buttons were turned over and remelted several times. For the 5:4 germanium compounds all of the rare-earth elements were investigated, with these exceptions: promethium, europium and ytterbium. In addition to these elements, holmium and thulium were not studied in the R_5Si_4 series.

Lattice constants of the various phases were obtained mainly from single-crystal oscillation and Weissenberg photographs. Filtered Cu $K\alpha$(= 1·5418 Å) radiation was used. In some instances, front-reflection lines in powder patterns prepared with Cr ($K\alpha$ = 2·2909 Å) radiation were used to obtain lattice constants. The latter were refined by means of the least-squares program of Heaton, Gvildys & Mueller (1964). Accuracy of the lattice constants derived from single-crystal photographs is estimated to be of the order of 0·5 %; those from powder patterns, 0·2 to 0·3 %.

Structural results

R_5Ge_4 *compounds*

When germanium is used as the combining element, all of the rare-earth metals studied form the orthorhombic 5:4 phase exhibited by Sm_5Ge_4. This behavior contrasts sharply with the behavior of the rare-earth monogermanides, for

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which three different structure types have been observed (Tharp, Smith & Johnson, 1966).

Crystallographic data pertinent to the orthorhombic 5:4 phase are as follows: probable space group, *Pnma* [from structure determination of Sm_5Ge_4 (Smith, Johnson & Tharp, 1967)]; the unit cell contains four R_5Ge_4 units. Excepting the cases for $R = Tm$ and Lu, the lattice constants (Table 1 and Fig. 1) follow a uniform lanthanide contraction so that the axial ratio, *a*:*b*:*c*, remains rather constant. More reliable determination of the lattice constants of Tm_5Ge_4 and Lu_5Ge_4 from powder patterns confirms the closer approach to equality of *a* and *c* for these compounds. The reason for this behavior is not clear.

Table 1. *Lattice constants of orthorhombic* R_5Ge_4 *compounds*

R	*a*	*b*	*c*	*V*
La	8·06 Å	15·47 Å	8·17 Å	1019 Å^3
Ce	7·96	15·21	8·04	973
Pr	7·90	15·11	7·99	954
Nd	7·86	15·06	7·93	939
Sm	7·75	14·94	7·84	908
Gd	7·69	14·75	7·76	880
Tb	7·62	14·66	7·72	862
Dy	7·58	14·54	7·65	843
Ho	7·54	14·51	7·63	835
Er	7·51	14·41	7·59	821
Tm	7·49	14·36	7·54	811
Lu	7·45	14·28	7·48	796
Y	7·63	14·68	7·68	860

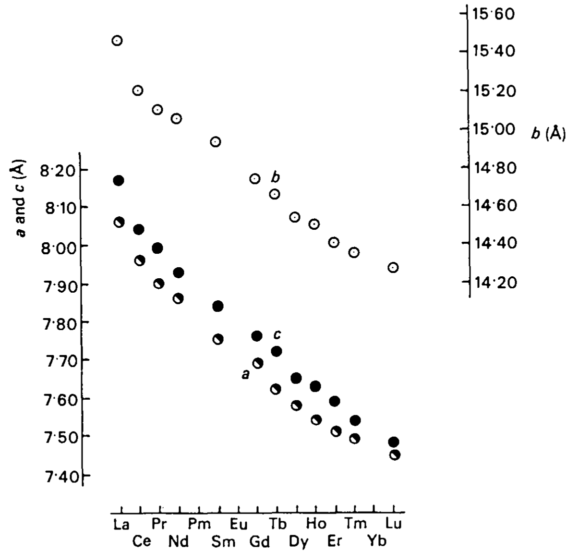

Fig. 1. Variation of the lattice constants of the orthorhombic R_5Ge_4 compounds.

R_5Si_4 *compounds*

The situation for the analogous silicon compounds is more complex. Single-crystal studies show that four of the lanthanide elements, terbium, dysprosium, erbium and yttrium, form the Sm_5Ge_4 type structure. Preparations with samarium and gadolinium yielded fine-grained samples from which no single crystals could be isolated. Powder patterns indicate the FeB type monosilicide (Hohnke & Parthé, 1966) as a major phase in the samarium and gadolinium preparations. The remaining lines could be indexed on the basis of the orthorhombic 5:4 phase; the lattice constants in Table 2 for Sm_5Si_4 and Gd_5Si_4 were obtained in this way.

Table 2. *Lattice constants of* R_5Si_4 *compounds*

R	Crystal class*	*a*	*b*	*c*	*V*
La	t	8·04 Å	8·04 Å	15·43 Å	997 Å^3
Ce	t	7·93	7·93	15·04	946
Pr	t	7·90	7·90	14·91	931
Nd	t	7·87	7·87	14·78	915
Sm	o	7·57	14·88	7·78	875
Gd	o	7·45	14·67	7·73	845
Tb	o	7·41	14·58	7·69	831
Dy	o	7·36	14·48	7·65	815
Er	o	7·27	14·32	7·58	789
Lu	m†	7·20	14·11	7·46	757
Y	o	7·39	14·52	7·64	819

* t = tetragonal; o = orthorhombic; m = monoclinic.
† Cell referred to has *c* axis unique; $\gamma = 92·1°$.

The silicide preparations with lanthanum, cerium, praseodymium and neodymium form tetragonal crystals. The diffraction effects are consistent with the space group $P4_12_12$ (or $P4_32_12$). The size and shape of the unit cell are similar to the orthorhombic 5:4 series; however, substantial differences in the reflection intensities indicate a different structure. It appears likely that this structure type is the same as that reported recently by Karpinsky & Evseev (1966) for Zr_5Si_4. Lattice constants for the tetragonal compounds were obtained from Debye–Scherrer patterns with

Table 3. *X-ray powder pattern for* Nd_5Si_4
Cr *Kα* radiation. Tetragonal: $a = 7·868$, $c = 14·78$ Å

hkl	$10^4 \sin^2\theta$ obs.	$10^4 \sin^2\theta$ calc.	*I* obs.	*hkl*	$10^4 \sin^2\theta$ obs.	$10^4 \sin^2\theta$ calc.	*I* obs.
112	672	664	*w*	204	1803	1808	*w*+
200	848	848	*w*	115	1925	1925	*s*
201	907	908	*m*	301	1970	1968	*w*
004	963	961	*w*+	214	2014	2020	*w*
210	1063	1060	*w*	302	2146	2148	*s*
202	1092	1088	*m*	223	2240	2236	*w*+
211	1125	1120	*m*−	205	2354	2349	*w*+
104	1173	1173	*m*	303	2451	2448	*w*
212	1305	1300	*vw*	116	2580	2585	*w*+
203 114	1388	1388 1385	*s*	224 322	2657 2990	2656 2996	*w*+ *vw*
213	1600	1600	*s*	314	3091	3080	*vw*
105	1716	1713	*w*+	216	3221	3221	*vw*
221	1756	1756	*vs*	117	3368	3366	*w*+

Cr radiation. The powder pattern observed for Nd_5Si_4 is given in Table 3.

The last member of the lanthanide elements, lutetium, forms a 5:4 compound that is monoclinic. This modification is a simple distortion of the orthorhombic phase as evidenced by a close similarity of reflection intensities between the two phases. To bring out the crystallographic similarity, the monoclinic cell chosen has the *c-axis unique*. The probable space group is $P2_1/a$. The extinction condition, $0kl$, $k+l=$ odd, observed in the orthorhombic phase is also retained in the monoclinic modification as a non-crystallographic condition. Crystals of this material are invariably twinned, the twin axis being the unique c axis.

A plot of the lattice constants (Fig. 2) shows several interesting features. As mentioned above, the orthorhombic and tetragonal compounds are of different structure types. Nevertheless, a smooth curve relates a-axis repeat distances in the tetragonal series with c-axis values in the orthorhombic and monoclinic series. Within the orthorhombic region, c/a ratios are larger than corresponding values in the germanide series. In further contrast, the c/a ratio becomes larger in going across the series rather than the converse as observed for the germanium compounds.

It may be remarked that the occurrence of three phases in the silicide series does not seem to follow from size effects. For the germanide compounds, the orthorhombic phase is stable for radius ratios (r_R/r_{Ge}) ranging from 1·37 (La_5Ge_4) to 1·27 (Lu_5Ge_4). [Atomic radii are taken from the compilation of Teatum, Gschneidner & Waber (1959)]. Against this behavior the orthorhombic phase in the silicide series is unstable at Lu_5Si_4 where the radius ratio is 1·32. For Sm_5Si_4 the ratio is 1·37; this could conceivably represent an upper limit for the orthorhombic phase. The radius ratio for tetragonal Zr_5Si_4, however, attains a value of 1·21. Thus, the occurrence of the tetragonal phase for the lighter (*i.e.* larger) lanthanide elements is not explained on the basis of size differences, if the usual valence of 3 is assumed for these elements.

R_5Si_3 *compounds*

Single crystals from the praesodymium preparation at this stoichiometry are body-centered tetragonal. The systematic extinctions and c/a axial ratio point to a $D8_l$ Cr_5B_3 structure type (space group $= I4/mcm$). The powder pattern of Ce_5Si_3 is quite similar to that of Pr_5Si_3; lattice constants obtained from these photographs are:

$$Ce_5Si_3 \; a=7{\cdot}89\pm0{\cdot}01,\; c=13{\cdot}78\pm0{\cdot}02 \text{ Å};\; V=858 \text{ Å}^3$$
$$Pr_5Si_3 \; a=7{\cdot}812\pm0{\cdot}005,\; c=13{\cdot}75\pm0{\cdot}01 \text{ Å};\; V=839 \text{ Å}^3 .$$

Table 4 shows the agreement between observed and calculated powder data for Pr_5Si_3, a Cr_5B_3 structure type being assumed. Intensities were calculated by means of the program of Smith (1963); no attempt was made to refine the positional parameters of the Cr_5B_3 structure (Bertaut & Blum, 1953). The powder pattern of La_5Si_3 given by Gladyshevskii *et al.* (1965) is readily indexed in terms of this structure type. Lattice constants for La_5Si_3 are:

$$a=7{\cdot}953,\; c=14{\cdot}04 \text{ Å};\; V=880 \text{ Å}^3 .$$

Thus, the structures of the R_5Si_3 compounds fall into at least two classes: a Cr_5B_3 type and an Mn_5Si_3 type. This behavior for the silicon compounds is in contrast with that of the analogous rare earth–germanium compounds for which only the Mn_5Si_3 structure type is found (Gladyshevskii, 1964).

Table 4. *X-ray powder data for* Pr_5Si_3

Space group: $I4/mcm$. Positional parameters as in Cr_5B_3. Chromium radiation ($K\alpha=2{\cdot}2909$ Å)

hkl	$10^4 \sin^2\theta$ obs.	$10^4 \sin^2\theta$ calc.	*I* obs.	*I* calc.
002	—	277	—	< 1
110	—	430	—	< 1
112	713	707	*w*+	20
200	867	860	*w*+	6
004	1115	1109	*m*−	9
202	1149	1137	*s*	27
211		1144		116
114	1547	1539	*m*	29
213	1708	1699	*vs*	100
220		1720		18
204	1978	1969	*s*	47
222	—	1997	—	1
310	2155	2150	*m*	62
312	—	2427	—	1
006	2504	2496	*m*	20
215	2821	2808	*vvw*	< 1
224	—	2829	—	< 1
321	2876	2864	*vvw*	< 1
116	—	2926	—	< 1
314	—	3259	—	< 1
206	3367	3356	*w*	2
323	—	3419	—	< 1
400	—	3440	—	2
402	3731	3717	*m*	2
411		3724		13
330	3875	3870	*vw*	9
332	4166	4147	*vvw*	6
226	4220	4216	*vvw*	4
413	4287	4279	*s*−	28
420		4300		9
008	—	4438	—	3
217	4477	4473	*s*−	32

We wish to thank Mr V. Silveira for the powder photography. This work was performed under the auspices of the U.S. Atomic Energy Commission.

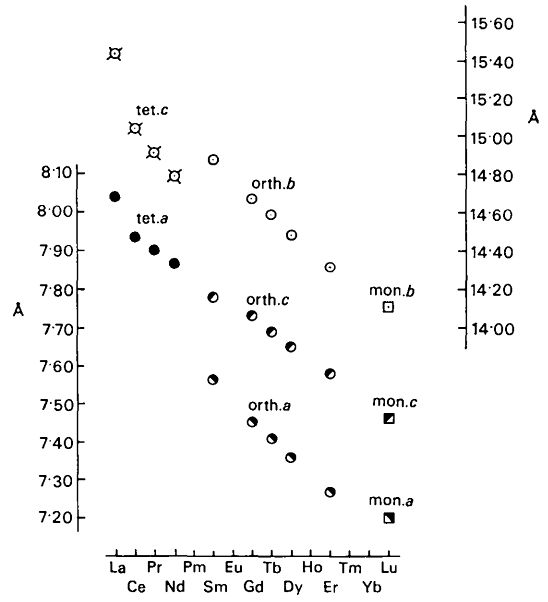

Fig. 2. Variation of the lattice constants of the R_5Si_4 compounds. Scale on left pertains to filled and half-filled symbols; scale on right pertains to open symbols.

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The crystal structure of the orthorhombic form of bis-(*N*-methylsalicylaldiminato)nickel.

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The crystal structure of the orthorhombic form of bis-(*N*-methylsalicylaldiminato)nickel has been determined. The space group is *Ibam* and the cell has dimensions $a=9{\cdot}22$, $b=24{\cdot}46$, $c=6{\cdot}58$ Å and contains 4 molecules. The crystal structure is essentially identical with that of the corresponding copper compound.

The crystal structure of the monoclinic form of bis-(*N*-methylsalicylaldiminato)nickel has been reported by Frasson, Panattoni & Sacconi (1959). We have now determined the crystal structure of the orthorhombic form, which is isomorphous with the α form of the corresponding copper compound (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961).

Green orthorhombic needles grown along [001] were obtained from Dr James Ferguson. Cell dimensions, determined from rotation and zero-level Weissenberg photographs, taken with Cu $K\alpha$ radiation and calibrated by superimposing the rotation pattern of sodium chloride ($a_0=5{\cdot}6894$ Å) on each photograph, are $a=9{\cdot}22(3)$, $b=24{\cdot}46(1)$, $c=6{\cdot}58(1)$ Å. Systematic absences of hkl for $h+k+l\neq 2n$, of $h0l$ for $h\neq 2n$, and of $0kl$ for $k\neq 2n$, indicate the space groups *Ibam* or *Iba*2. There are four molecules in the cell.

A crystal of dimensions 0·1 mm × 0·06 mm × 0·8 mm was used for collection of intensities of $hk0$ through $hk3$. Because of the great similarity of the distribution of intensities between $hk0$ and $hk2$ and between $hk1$ and $hk3$, only the $hk0$ and $hk1$ intensities were measured. The photographs were taken on a Nonius integrating-Weissenberg camera and the intensities were measured as previously described (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961). 219 independent reflections were examined, of which 48 were found to be too weak to be measured. Lorentz and polarization factors were applied, but no corrections were made for absorption or anomalous dispersion.

The structure was refined by full-matrix least-squares calculations using the program of Busing & Levy (1959) as adapted by Stewart (1964). The function minimized was $\Sigma\, w(F_o-F_c)^2$ and all reflections were given equal weight except that, in each cycle, unobserved reflections with $F_c<F_o$ were given zero weight. The initial parameters used for the non-hydrogen atoms were those from the copper compound (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961). After five cycles, R was 0·080, where $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, with summation over the observed reflections only. At this point, hydrogen atom positions were calculated, and a plot of $\log F_o/F_c$ *vs* I_c indicated that the 110, 121 and 141 reflections were affected by secondary extinction. A set of four additional least-squares cycles, including the contributions of the hydrogen atoms but not refining their parameters, and omitting the reflections 110, 121 and 141, reduced R to its final value of 0·070. In the final cycle, all parameter shifts were less than one standard deviation. The final values of the parameters and their estimated standard deviations are listed in Table 1, while the bond lengths and angles are listed in Table 2.

Table 1. *Final values of parameters*

	$x/a\times 10^4$	$y/b\times 10^4$	$z/c\times 10^4$	$B\times 10$
Ni	0	0	0	32 (1)
N	−1222 (13)	635 (4)	0	32 (3)
O	1694 (9)	406 (3)	0	27 (2)
C(1)	1892 (20)	948 (5)	0	32 (4)
C(2)	3287 (16)	1146 (6)	0	36 (4)
C(3)	3539 (18)	1708 (6)	0	49 (5)
C(4)	2456 (17)	2063 (6)	0	39 (4)
C(5)	1036 (17)	1889 (6)	0	39 (4)
C(6)	705 (16)	1312 (6)	0	35 (4)
C(7)	−778 (14)	1145 (5)	0	28 (3)
C(8)	−2836 (14)	563 (5)	0	26 (3)
H(1)	4125	887	0	36
H(2)	4561	1846	0	49
H(3)	2673	2464	0	39
H(4)	232	2164	0	39
H(5)	1535	1438	0	28
H(6)	3175	175	0	26
H(7)	−3233	746	1241	26