Table 3. *Interatomic distances* (Å) *and angles* (°)

GeF$_6$ octahedron

Ge–F(1)	1·842 (2)	Ge–F(3),F(3^i)	1·762 (1)
Ge–F(2)	1·789 (2)	Ge–F(4),F(4^i)	1·793 (1)
F(1)–Ge–F(2)	176·1 (1)	F(3)–Ge–F(4)	90·0 (1)
F(1)–Ge–F(3)	89·4 (1)	F(3)–Ge–F(3^i)	90·1 (1)
F(1)–Ge–F(4)	87·8 (1)	F(3)–Ge–F(4^i)	177·2 (1)
F(2)–Ge–F(3)	93·3 (1)	F(4)–Ge–F(4^i)	89·8 (1)
F(2)–Ge–F(4)	89·5 (1)		

N$_2$H$_6^{2+}$ ion

N–N^{ii}	1·428 (2)	N–H(1)	0·85 (3)
		N–H(2)	0·83 (3)
		N–H(3)	0·83 (3)
N^{ii}–N–H(1)	105 (2)	H(1)–N–H(2)	121 (3)
N^{ii}–N–H(2)	110 (2)	H(1)–N–H(3)	94 (3)
N^{ii}–N–H(3)	108 (2)	H(2)–N–H(3)	118 (3)

Water molecule

O–H(4)	0·88 (4)	H(4)–O–H(5)	118 (4)
O–H(5)	0·85 (5)	H(2)–O–H(4)	115 (2)
O···H(2),H(2^i)	1·93 (3)	H(2)–O–H(5)	102 (2)
		H(2)–O–H(2^i)	102 (2)

Hydrogen-bond distances and angles

D–H···A	D–A	D–H	H···A	D–H···A
N–H(1)···F(2^{iii})	2·876 (2)	0·85 (3)	2·42 (3)	114 (2)
N–H(1)···F(3^{iv})	2·698 (3)	0·85 (3)	2·23 (3)	115 (2)
N–H(1)···F(4^v)	2·763 (2)	0·85 (3)	2·03 (3)	144 (3)
N–H(2)···O	2·757 (2)	0·83 (3)	1·94 (3)	170 (3)
N–H(3)···F(^{vi})	2·847 (2)	0·83 (3)	2·15 (3)	142 (3)
N–H(3)···F(3^{iv})	2·698 (2)	0·83 (3)	2·19 (3)	120 (2)
O–H(4)···F(1^{vii})	2·877 (2)	0·88 (4)	2·00 (4)	174 (4)
O–H(5)···F(2)	2·731 (3)	0·85 (5)	1·93 (5)	155 (5)

Symmetry code

(i)	$x, \frac{1}{2} - y, z$	(v) $-1 + x, y, z$
(ii)	$-x, -y, 1 - z$	(vi) $1 - x, -y, 1 - z$
(iii)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$	(vii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$
(iv)	$-\frac{1}{2} - x, -y, \frac{1}{2} + z$	

in N$_2$H$_6$SO$_4$ (Jönsson & Hamilton, 1970) and N$_2$H$_6$[SiF$_6$] (Frlec, Gantar, Golič & Leban, 1980). The F atoms are octahedrally arranged around the Ge atom forming a slightly distorted octahedron. The Ge–F lengths, ranging from 1·762 (1) to 1·842 (2) Å, are close to the reported values of 1·71 – 1·80 (2) Å in, for example, Ge$_5$F$_{12}$ (Taylor & Wilson, 1973).

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Rhodium Scandium Disilicide with an Ordered YZn$_3$-Type Structure

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Abstract. ScRhSi$_2$, *Pnma*, $a = 6·292$ (4), $b = 4·025$ (4), $c = 9·517$ (5) Å, $Z = 4$, $D_x = 5·62$ (1) Mg m^{-3}, μ(Mo $K\alpha$) = 10 mm^{-1}, $F(000) = 376$. This compound crystallizes with an ordered version of the YZn$_3$ structure type with the Rh and Si atoms occupying the corresponding Zn sites. The final weighted $R = 0·052$ for 536 reflections. It is shown that the structure types YZn$_3$, ScRhSi$_2$, CeZn$_3$, Re$_3$B and MgAl$_2$Cu are all geometrically related, the last three being higher-symmetry versions with space group *Cmcm*. Furthermore, some geometrical relationships

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Table 1. *Structural data for* Re$_3$B *derivative structures (space group Cmcm) compared with those for* YZn$_3$ *and* ScRhSi$_2$ *(space group Pnma)*

The isotropic temperature factors of ScRhSi$_2$ are expressed as $T = \exp[-2\pi^2 \, 10^{-2} \, U(2 \sin \theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

Re$_3$B Cmcm	MgAl$_2$Cu Cmcm	CeZn$_3$ Cmcm	YZn$_3$ Pnma	ScRhSi$_2$ Pnma	U (Å^2)
$a = 2.890$ Å $b = 9.313$ $c = 7.258$	$a = 4.01$ Å $b = 9.25$ $c = 7.15$	$a = 4.627$ Å $b = 10.437$ $c = 6.644$	$a = 6.690$ Å $b = 4.405$ $c = 10.111$	$a = 6.292$ (4) Å $b = 4.025$ (4) $c = 9.517$ (5)	
4 Re in 4(c) $y = 0.0738$	4 Mg $y = 0.072$	4 Ce $y = 0.10$	4 Y in 4(c) $x = 0.2773$ $z = 0.3387$	4 Sc $x = 0.2385$ (4) $z = 0.3181$ (3)	0.52 (5)
8 Re in 8(f) $y = 0.3655$ $z = 0.062$	8 Al $y = 0.356$ $z = 0.056$	8 Zn $y = 0.38$ $z = 0.055$	4 Zn(3) in 4(c)$x = 0.5362$ $z = 0.8956$	4 Rh $x = 0.5832$ (2) $z = 0.9008$ (1)	0.27 (2)
			4 Zn(2) in 4(c)$x = 0.9162$ $z = 0.8549$	4 Si(2) $x = 0.9573$ (6) $z = 0.8413$ (4)	0.51 (7)
4 B in 4(c) $y = 0.756$	4 Cu $y = 0.778$	4 Zn $y = 0.81$	4 Zn(1) in 4(c)$x = 0.2152$ $z = 0.0449$	4 Si(1) $x = 0.2318$ (7) $z = 0.0282$ (4)	0.41 (7)
Origin shift from published data by $0\frac{1}{2}\frac{1}{2}$ (Aronsson, Backman & Rundqvist, 1960)	Perlitz & Westgren (1943)	Transformed from *Pnma* with shift of origin by $\frac{1}{4}\frac{1}{4}0$ (Bruzzone, Fornasini & Merlo, 1970)	Michel & Ryba (1968)	Numbering of Si atoms was chosen to agree with numbering of Zn in YZn$_3$ (this work)	

can be found between ScRhSi$_2$ and the TiNiSi structure type.

Introduction. In the course of a search for new superconducting compounds the partial phase diagram Sc–Rh–Si (>40 at.% Si) has been studied by Braun, Burri & Rinderer (1979). They determined the compositions of nine ternary phases and reported a tetragonal cell for Sc$_5$Rh$_4$Si$_{10}$ and an orthorhombic cell for ScRhSi$_2$. The structure of Sc$_5$Rh$_4$Si$_{10}$ has been solved by Braun, Yvon & Braun (1980), who found a new structure type with space group *P4/mbm*. We report here the structure of orthorhombic ScRhSi$_2$, a phase which does not show any superconductivity above 1 K.

The alloy was prepared by arc melting under an argon atmosphere from elements of high purity. A single crystal of 80 μm mean diameter was isolated from a crushed ingot with starting composition equivalent to ScRhSi$_2$ and annealed at 1270 K for three days. Cell parameters were obtained by least-squares refinement of the 2θ values of 20 reflections. According to the Laue class (*mmm*) and the conditions limiting possible reflections (0kl: $k + l = 2n$; hk0: $h = 2n$) the possible space groups are *Pnma* or *Pn2$_1$a*. Data collection was carried out on a four-circle diffractometer (Philips PW 1100) in the ω–2θ mode with graphite-monochromated Mo $K\alpha$ radiation, out to a limit of sin $\theta/\lambda = 0.85$ Å^{-1}, yielding 680 independent reflections. The structure was solved from a Patterson map. A scale factor, and positional parameters and isotropic temperature factors were refined in *Pnma* with the full-matrix least-squares program *CRYLSQ* (XRAY system, 1976). Scattering factors were taken

Table 2. *Interatomic distances* (Å) *in* ScRhSi$_2$ *up to* 3.53 Å

E.s.d.'s are given in parentheses. CN indicates the coordination number as defined in the text.

Sc– Si(1)	2.759 (5)		Rh– Si(2)	2.421 (5)	
–2Si(2)	2.786 (4)		–2Si(1)	2.421 (3)	
–2Si(2)	2.805 (4)		– Si(2)	2.437 (4)	
–2Si(1)	2.843 (4)	CN = 14	– Si(1)	2.522 (4)	CN = 12
– Rh	2.848 (4)		– Sc	2.848 (4)	
–2Rh	2.961 (3)		–2Rh	2.951 (2)	
–2Rh	3.106 (3)		–2Sc	2.961 (3)	
–2Sc	3.403 (5)		–2Sc	3.106 (3)	
– Si(1)	3.431 (5)				
– Si(1)	3.508 (5)				
– Si(2)	3.521 (5)				
Si(1)–2Rh*	2.421 (3)		Si(2)– Rh	2.421 (5)	
– Si(2)	2.479 (6)		– Rh	2.437 (4)	
– Rh	2.522 (4)		– Si(1)	2.479 (6)	
–2Si(2)*	2.647 (4)	CN = 9	–2Si(1)*	2.647 (4)	CN = 9
– Sc	2.759 (5)		–2Sc*	2.786 (4)	
–2Sc*	2.843 (4)		–2Sc*	2.805 (4)	
– Sc	3.431 (5)				
– Sc	3.508 (5)				

* Atoms which belong to deformed trigonal prisms.

from *International Tables for X-ray Crystallography* (1974) and intensities were corrected for spherical absorption. Refinement of the 13 structural parameters with 536 reflections with $|F| > 3\sigma_F$ led to $R = \sum|\Delta F|/\sum|F_o| = 0.062$ ($R_w = 0.052$ with $w = 1/\sigma_F^2$).*

The final positional and thermal parameters are listed in the last column of Table 1, interatomic distances in Table 2.

Discussion. Coordination numbers for the atoms in $ScRhSi_2$ have been determined from the interatomic distances given in Table 2 and the gap criterion limit (Bruzzone, Fornasini & Merlo, 1970). Sc atoms have a coordination number of 14, consisting of 7 Si, 5 Rh and 2 Sc. Rh atoms are coordinated by 12 atoms (5 Si, 5 Sc, 2 Rh) in the form of a distorted cubo-octahedron. Both Si(1) and Si(2) have the coordination number 9 and have nearly the same geometrical surroundings. The neighbouring atoms are at the six vertices of trigonal prisms with three additional atoms outside the rectangular faces of the prisms. Si(1) is surrounded by 3 Sc, 3 Si(2) and 3 Rh and Si(2) by 4 Sc, 3 Si(1) and 2 Rh. With 50 at.% Si the presence of Si–Si bonds is not unlikely. However, in comparison with other silicides the Si–Si distances in $ScRhSi_2$ are rather large.

The structure of $ScRhSi_2$ (Fig. 1e) may be considered as an ordered version of the YZn_3 type (Michel & Ryba, 1968) (Fig. 1d). From Table 1 one can conclude that the Zn(1), Zn(2) and Zn(3) sites of YZn_3 correspond to the Si(1), Si(2) and Rh sites of $ScRhSi_2$. In Fig. 1(d) and (e) for comparison the outlines have been drawn of deformed trigonal prisms which are formed by 2 Y and 4 Zn and centred by Zn atoms or which are built up by 2 Sc, 2 Rh and 2 Si(2) and centred by Si(1) atoms, respectively. These prisms are base- and top-linked to form columns parallel to **b**. Similar prisms are observed in $CeZn_3$ which was described in the higher-symmetry space group $Amma$ ($\equiv Cmcm$) by Bruzzone, Fornasini & Merlo (1970). The

reason for this change to a non-primitive space group is that the prisms in $CeZn_3$ are more symmetrical than in YZn_3 [adjustable parameters referred to the YZn_3 structure with space group $Pnma$: $x_{Ce} = \frac{1}{4}$; $x_{Zn(3)} - \frac{1}{2} = 1 - x_{Zn(2)}$; $z_{Zn(3)} = z_{Zn(2)}$ and $x_{Zn(1)} = \frac{1}{4}$]. The $CeZn_3$ structure itself is geometrically related to the Re_3B and $MgAl_2Cu$ types which differ in the distribution of the different atoms on the available sites. In Re_3B the trigonal prisms are formed by 6 Re and centred by B atoms whereas in $MgAl_2Cu$ they are built up by 2 Mg and 4 Al and centred by Cu atoms.

If the structure of $ScRhSi_2$ is considered as a derivative structure of the Re_3B type the question arises why this compound does not adopt the higher-symmetry $MgAl_2Cu$ type with Sc and Si forming the trigonal prism and Rh atoms centring it. This type is, for example, formed with YAl_2Ni (Rykhal, Zarechnyuk & Yarmolyuk, 1972) and $GdAl_2Ni$ (Rykhal, Zarechnyuk & Marich, 1978) where Ni atoms centre the trigonal prisms. A possible reason could be that both Si(1) and Si(2) tend to adopt a coordination of 9 and for that purpose prefer to be at the centre of a tricapped trigonal prism as part of their overall coordination. As can be seen from a study of Fig. 1(e) and Table 2 this type of environment is achieved better in $Pnma$ than in $Cmcm$. The trigonal prisms which are formed by 4 Sc and 2 Si and centred by Si(2) atoms (one of which is indicated with dotted lines) are more symmetrical than the Si(1)-centred trigonal prism formed by 2 Sc, 2 Rh and 2 Si atoms (drawn with full lines).

In Fig. 2(a) the $ScRhSi_2$ structure is redrawn indicating the prisms around Si(2) atoms only. One can see that sheets of Si-centred prisms are formed whose
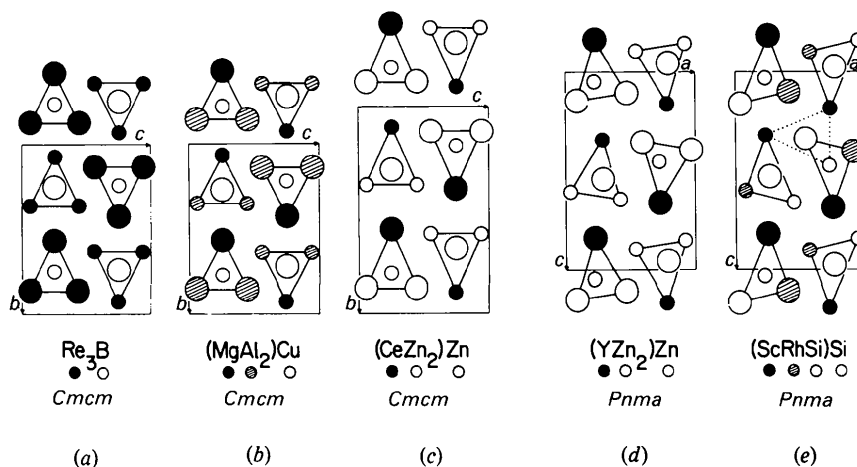

Fig. 1. The geometrical relationship between the Re_3B, $MgAl_2Cu$, $CeZn_3$, YZn_3 and $ScRhSi_2$ structure types. Small circles are at $x = 0$ for $Cmcm$ and at $y = \frac{1}{4}$ for $Pnma$. Large circles are at $x = \frac{1}{2}$ for $Cmcm$ and at $y = \frac{3}{4}$ for $Pnma$. For $ScRhSi_2$ the Si(1) atoms are at the centres of trigonal prisms drawn with full lines, the other open circles corresponding to Si(2) atoms. The trigonal prism indicated with dotted lines is centred by a Si(2) atom. In the chemical formulae the elements forming the trigonal prisms are written in parentheses, those centring the prisms outside.
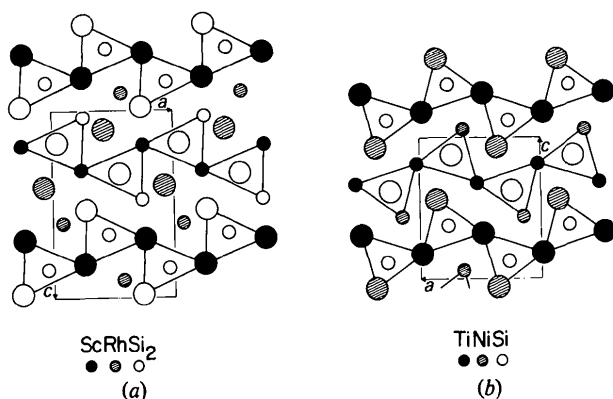
Fig. 2. Comparison between the ScRhSi$_2$ and the TiNiSi types (*Pnma* setting).

arrangement resembles that found in the TiNiSi type (Shoemaker & Shoemaker, 1965) (Fig. 2*b*), of which ScNiSi and ScCoSi (Kotur & Bodak, 1977) constitute a subtype. The geometrical form of the coordination polyhedra for the Si atoms is similar in both structures but only in ScRhSi$_2$ do the polyhedra contain Si atoms. The geometrical environment of Rh in ScRhSi$_2$ is similar to that of Ni in TiNiSi.

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Trirhodium Scandium Heptasilicide and Triiridium Scandium Heptasilicide with a New Rhombohedral Structure Type

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Abstract. ScRh$_3$Si$_7$: $a = 7.5056$ (6), $c = 19.691$ (4) Å, $D_x = 5.706$ Mg m^{-3}, μ(Mo $K\alpha$) = 9.6 mm^{-1}, $F(000)$ = 1524; ScIr$_3$Si$_7$: $a = 7.5010$ (2), $c = 19.909$ (1) Å, $D_x = 8.403$ Mg m^{-3}, μ(Mo $K\alpha$) = 67 mm^{-1}, $F(000) = 2100$. ScRh$_3$Si$_7$ and ScIr$_3$Si$_7$ crystallize with a new rhombohedral structure type in space group $R\bar{3}c$, $Z = 6$. For ScRh$_3$Si$_7$ (ScIr$_3$Si$_7$) the final $R = 0.037$ (0.072) for 272 (250) reflections. The Rh and Sc arrangement found in ScRh$_3$Si$_7$ is similar to that found in the PdF$_3$-type structure. Sc (Pd) are at the centres of octahedra formed by a hexagonal close-packed array of Rh (F) atoms. The crystal structures of ScRh$_3$Si$_7$ and ScIr$_3$Si$_7$ are stabilized by strong Rh–Si and Ir–Si interactions with each Si surrounded by three Rh or Ir atoms.

Introduction. Of the nine ternary phases found in the Si-rich part of the Sc–Rh–Si phase diagram (Braun, Burri & Rinderer, 1979), two have been analysed structurally. Sc$_5$Rh$_4$Si$_{10}$ crystallizes with a new tetragonal structure type (Braun, Yvon & Braun, 1980) and orthorhombic ScRhSi$_2$ is an ordered version of the YZn$_3$ type (Chabot, Braun, Yvon & Parthé, 1981). The phase on which we report here was given the composition ScRh$_3$Si$_6$ by Braun, Burri & Rinderer