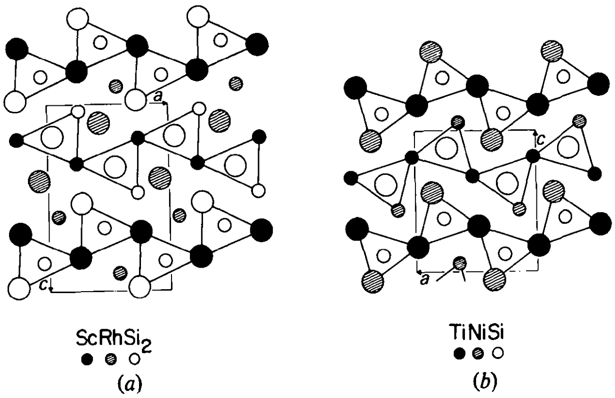

Fig. 2. Comparison between the $\mathrm{ScRhSi_2}$ and the TiNiSi types (*Pnma* setting).

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 $\mathrm{ScRhSi_2}$ do the polyhedra contain Si atoms. The geometrical environment of Rh in $\mathrm{ScRhSi_2}$ 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

BY B. CHABOT, N. ENGEL AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

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Abstract. $\mathrm{ScRh_3Si_7}$: $a = 7{\cdot}5056$ (6), $c = 19{\cdot}691$ (4) Å, $D_x = 5{\cdot}706$ Mg m^{-3}, μ(Mo $K\alpha$) = 9·6 mm^{-1}, $F(000) = 1524$; $\mathrm{ScIr_3Si_7}$: $a = 7{\cdot}5010$ (2), $c = 19{\cdot}909$ (1) Å, $D_x = 8{\cdot}403$ Mg m^{-3}, μ(Mo $K\alpha$) = 67 mm^{-1}, $F(000) = 2100$. $\mathrm{ScRh_3Si_7}$ and $\mathrm{ScIr_3Si_7}$ crystallize with a new rhombohedral structure type in space group $R\bar{3}c$, $Z = 6$. For $\mathrm{ScRh_3Si_7}$ ($\mathrm{ScIr_3Si_7}$) the final $R = 0{\cdot}037$ (0·072) for 272 (250) reflections. The Rh and Sc arrangement found in $\mathrm{ScRh_3Si_7}$ is similar to that found in the $\mathrm{PdF_3}$-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 $\mathrm{ScRh_3Si_7}$ and $\mathrm{ScIr_3Si_7}$ 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. $\mathrm{Sc_5Rh_4Si_{10}}$ crystallizes with a new tetragonal structure type (Braun, Yvon & Braun, 1980) and orthorhombic $\mathrm{ScRhSi_2}$ is an ordered version of the $\mathrm{YZn_3}$ type (Chabot, Braun, Yvon & Parthé, 1981). The phase on which we report here was given the composition $\mathrm{ScRh_3Si_6}$ by Braun, Burri & Rinderer

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(1979). However, the crystal structure analysis revealed the true composition to be $ScRh_3Si_7$. $ScRh_3Si_7$ does not show any superconductivity (H. F. Braun, personal communication).

Sc–Rh–Si and Sc–Ir–Si alloys were prepared from elements of high purity (sublimed Sc 99·95% and 99·9% for Rh and Ir) by arc-melting techniques under an argon atmosphere.

Single crystals were isolated from crushed melts with starting composition 1:3:6. The true composition of the phase was revealed later to be 1:3:7. The mean diameter for the single crystal of $ScRh_3Si_7$ was 80 μm and for $ScIr_3Si_7$ 60 μm. Cells are triple hexagonal and their parameters were obtained by least-squares refinement of the 2θ values of 50 reflections. According to the Laue class ($\bar{3}m$) and the conditions limiting possible reflections ($hkil$: $-h+k+l=3n$; $h\bar{h}0l$: $l=2n$) the possible space groups are $R3c$ or $R\bar{3}c$. Data collections for $ScRh_3Si_7$ and $ScIr_3Si_7$ were 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 $\sin\theta/\lambda = 0{\cdot}7$ Å^{-1}, yielding 314 (305) independent reflections. The structure was solved from a Patterson map with the Rh data set. A difference synthesis led us to introduce an extra Si atom, resulting in the composition 1:3:7. Scale factors, positional parameters and isotropic parameters refined satisfactorily in $R\bar{3}c$ for the two compounds with the full-matrix least-squares program *CRYLSQ* (XRAY system, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and intensities were corrected in both cases for spherical absorption. Refinements for nine structural parameters were obtained from 272 (250) reflections with $|F_o| > 3\sigma(F_o)$. $R = \sum|\Delta F|/\sum|F_o| = 0{\cdot}037$ for $ScRh_3Si_7$ after correction of the structure factors for isotropic secondary extinction and 0·072 for $ScIr_3Si_7$ (without extinction correction).[*] Atomic parameters are given in Table 1 and interatomic distances in Table 2.

Table 1. *Point positions for* $ScRh_3Si_7$ *and* $ScIr_3Si_7$ (*space group* $R\bar{3}c$, *hexagonal axes*)

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

	x	y	z	U (Å^2)
$ScRh_3Si_7$				
Sc in 6(*b*)	0	0	0	0·69 (8)
Rh in 18(*e*)	0·3223 (2)	0	$\frac{1}{4}$	0·39 (3)
Si(1) in 36(*f*)	0·5380 (5)	0·6786 (4)	0·0302 (2)	0·73 (6)
Si(2) in 6(*a*)	0	0	$\frac{1}{4}$	0·8 (1)
$ScIr_3Si_7$				
Sc in 6(*b*)	0	0	0	1·2 (3)
Ir in 18(*e*)	0·3234 (3)	0	$\frac{1}{4}$	0·45 (5)
Si(1) in 36(*f*)	0·539 (1)	0·680 (1)	0·029 (1)	0·9 (1)
Si(2) in 6(*a*)	0	0	$\frac{1}{4}$	1·1 (4)

Table 2. *Interatomic distances* d (Å) *and rounded values* Δ ($\equiv d - \sum r$) (Å) *for* $ScRh_3Si_7$ *and* $ScIr_3Si_7$ *up to* $1{\cdot}3\sum r$

The atomic radii (r) used for Sc, Si, Rh and Ir are 1·62, 1·32, 1·34 and 1·36 Å respectively. E.s.d.'s are given in parentheses.

$ScRh_3Si_7$	d	Δ	$ScIr_3Si_7$	d	Δ
Sc –6Rh	3·027 (1)	+0·07	Sc –6Ir	3·033 (2)	+0·05
–6Si(1)	3·075 (3)	+0·14	–6Si(1)	3·12 (1)	+0·18
–6Si(1)	3·135 (4)	+0·20	–6Si(1)	3·12 (1)	+0·18
Rh –2Si(1)	2·417 (4)	–0·24	Ir –2Si(1)	2·41 (1)	–0·27
–1Si(2)	2·419 (1)	–0·24	–2Si(1)	2·42 (1)	–0·26
–2Si(1)	2·421 (3)	–0·24	–1Si(2)	2·426 (2)	–0·25
–2Si(1)	2·481 (3)	–0·18	–2Si(1)	2·507 (9)	–0·17
–2Sc	3·027 (1)	+0·07	–2Sc	3·033 (2)	+0·05
Si(1)–1Rh	2·417 (4)	–0·24	Si(1)–1Ir	2·41 (1)	–0·27
–1Rh	2·421 (3)	–0·24	–1Ir	2·42 (1)	–0·26
–1Rh	2·481 (3)	–0·18	–1Ir	2·507 (9)	–0·17
–2Si(1)	2·587 (5)	–0·05	–2Si(1)	2·59 (2)	–0·05
–1Si(1)	2·679 (4)	+0·04	–1Si(2)	2·69 (2)	+0·05
–1Si(2)	2·688 (3)	+0·05	–1Si(1)	2·72 (1)	+0·08
–1Si(1)	2·720 (5)	+0·08	–1Si(1)	2·72 (1)	+0·08
–1Sc	3·075 (3)	+0·14	–1Sc	3·12 (1)	+0·18
–1Sc	3·135 (3)	+0·20	–1Sc	3·12 (1)	+0·18
–2Si(1)	3·300 (6)	+0·66	–2Si(1)	3·28 (2)	+0·64
–1Si(2)	3·353 (4)	+0·71	–1Si(2)	3·37 (1)	+0·73
Si(2)–3Rh	2·419 (1)	–0·24	Si(2)–3Ir	2·426 (2)	–0·25
–6Si(1)	2·688 (3)	+0·05	–6Si(1)	2·69 (1)	+0·05
–6Si(1)	3·353 (4)	+0·71	–6Si(1)	3·37 (1)	+0·73

Discussion. A convenient way to describe the crystal structure of $ScRh_3Si_7$ is to concentrate at first only on the Rh and Sc arrangement. The Rh atoms alone form a hexagonal close-packed (h.c.p.) arrangement with six layers per unit cell stacked along **c**. Each Rh double

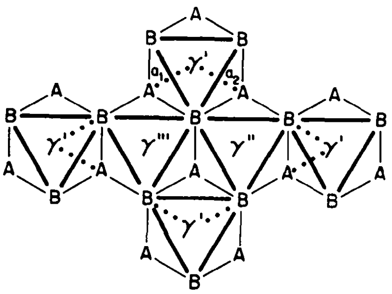

Fig. 1. Projection of Rh and Sc sites along [0001]. The Rh atoms are hexagonal close-packed (stacking positions A and B) while the Sc atoms occupy one third of the available octahedral interstices (stacking positions γ', γ'', γ'''). If we assume the Rh A layer to be at height $-\frac{1}{12}$ and the Rh B layer to be at $+\frac{1}{12}$, the Sc atoms occupy site γ' at height 0. The stacking of the Rh and Sc atoms in the complete structure can be described by the sequence $A\gamma'B\gamma''A\gamma'''B\gamma'A\gamma''B\gamma'''$ where the distance between neighbouring levels corresponding to neighbouring letters is $\frac{1}{24}$ of the **c** translation.

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[*] Lists of structure factors for $ScRh_3Si_7$ and $ScIr_3Si_7$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35830 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

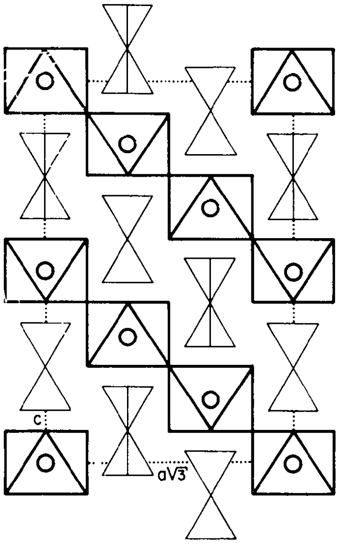

Fig. 2. Arrangement of the Sc-centred Rh octahedra (heavy lines) and the Si double tetrahedra (thin lines) centred on $(11\bar{2}0)$ in $ScRh_3Si_7$. Only the Sc atoms (small circles) and the Si(2) atoms at the middle of the double tetrahedra are exactly on $(11\bar{2}0)$. Only the front faces of the polyhedra are shown. Octahedra and double tetrahedra appear in two different positions which differ by a rotation of 180° around [0001].

layer may be described as a sheet of edge-connected Rh octahedra and one out of three of these octahedral sites is occupied by a Sc atom. Fig. 1 shows that the distribution of the Sc atoms on the available octahedral sites in the h.c.p. arrangement of Rh atoms can be expressed by the sequence $A\gamma'B\gamma''A\gamma'''B\gamma'A\gamma''B\gamma'''$. Roman letters refer to the Rh positions and Greek letters to Sc positions, the primes being used to differentiate between the three possible octahedral interstitial sites per *AB* double layer. A binary structure corresponding to the $ScRh_3$ arrangement in $ScRh_3Si_7$ is already known for PdF_3 (Hepworth, Jack, Peacock & Westland, 1957). The ideal c/a ratio for the PdF_3 type is $2\sqrt{2} = 2{\cdot}818$. However, for $ScRh_3Si_7$, owing to the presence of the Si atoms, we find 2·62.

Si atoms centre one out of two of the triangular faces of the empty Rh octahedra. Two of these octahedra share a common face which is centred by a Si(2) atom. The Si atom grouping can be conveniently represented as double tetrahedra having one apex in common. Only Si(2) is common to both tetrahedra, the remaining six atoms being Si(1). The arrangement of Sc-centred Rh octahedra and Si double tetrahedra in the $(11\bar{2}0)$ plane is shown in Fig. 2.

The Rh atom itself is surrounded by a more complicated coordination polyhedron consisting of two Sc and seven Si atoms. The geometrical arrangement of the seven Si around the Rh atoms is similar to the Si surrounding of Rh in RhSi with the FeSi structure type (Engström & Johnsson, 1965).

The $ScRh_3Si_7$-type structure seems to be dominated by the short Rh—Si distances (Table 2). These contractions in the distances of nearly 0·25 Å with respect to the sum of the metallic radii are not unusual. A similar shortening of bonds has been reported, for example, by Engström (1970) in binary platinum silicides. On the other hand, no such interactions exist between Sc and Si atoms. In the binary transition-metal (*T*) silicides the *T*—Si contractions (Aronsson, 1966) become generally more pronounced the higher the group number of the *T* partner. This rule, which is effectively valid for the $ScRh_3Si_7$-type structure, is no longer true for other ternary compounds such as $Sc_5Co_4Si_{10}$ (Braun, Yvon & Braun, 1980) or $ScRhSi_2$ (Chabot, Braun, Yvon & Parthé, 1981). In both these cases strong interactions exist between Si and Sc as well as between Si and the other *T* elements.

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