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$Sc_7Re_4Si_{10}$, a Ternary Substitution Variant of the Tetragonal $Ho_{11}Ge_{10}$ Type

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Abstract. $Sc_7Re_{4-x}Si_{10+x}$ [$x = 0.65$ (5)], $M_r = 1237.6$, tetragonal, $tI84$, $I4/mmm$, $a = 9.8123$ (4), $c = 14.274$ (2) Å, $V = 1374.3$ (3) Å^3, $Z = 4$, $D_x = 5.980$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 35.0$ mm^{-1}, $F(000) = 2189$, $T = 293$ K, $wR = 0.046$ for 607 unique contributing reflections. The $Sc_7Re_{4-x}Si_{10+x}$ ($x = 0.65$) structure can be considered as a substitution variant of the $Ho_{11}Ge_{10}$ type. A similar substitution variant has been reported for $Sc_7Cr_{4+x}Si_{10-x}$ ($x = 0.8$) with a different composition and a slightly different site occupation. The $Sc_7Re_4Si_{10}$ structure can be built up of 5.3 Å-thick segments cut from the tetragonal $Zr_4Co_4Ge_7$ structure and monoatomic Si layers. Segments of the $Sc_7Re_4Si_{10}$ structure can be used to build up the $YbMo_2Al_4$ structure.

Introduction. The Sc–Re–Si phase diagram has been studied by Pecharskii (1979; cited by Rogl, 1984) who found five ternary phases of which three crystal structures have already been determined: tetragonal $Sc_2Re_3Si_4$ with an ordered ternary substitution variant of the Zr_5Si_4 type (Pecharskii, Bodak & Gladyshevskii, 1978); monoclinic $Sc_3Re_2Si_4$ (formerly $Sc_3Re_2Si_3$) (Chabot & Parthé, 1985) and orthorhombic $Sc_5Re_8Si_{12}$ (formerly $ScRe_2Si_3$) (Chabot & Parthé, 1987). We report here on the structure of the phase originally denoted by Pecharskii as $Sc_8Re_3Si_9$.

Experimental. The sample of nominal composition $Sc_8Re_3Si_9$ was prepared by arc melting under argon atmosphere (Sc 99.99, Re 99.99 and Si 99.999%). The weight loss was 1.0%. The sample was annealed at 1073 K for 60 d in a silica tube under 40 kPa argon atmosphere. The single crystals were found in both the annealed sample and the unannealed sample. A single crystal with regular shape [±(001): 0.024 mm, ±(110): 0.048 mm, (1̄11): 0.024 mm, (410): 0.016 mm] obtained from the annealed sample was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The cell parameters were refined from 2θ values of 37 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $30 \le 2\theta \le 45°$) using the program *PARAM*. 2321 reflections were collected out to $(\sin\theta)/\lambda = 0.70$ Å^{-1} ($-13 \le h \le 13$, $-13 \le k \le 13$, $0 \le l \le 20$) in the ω–2θ scan mode, yielding 607 unique reflections ($R_{int} = 0.028$). Two standard reflections (125 and 1̄2̄5) were measured with maximum intensity variations 1.1 and 1.2% respectively. Absorption corrections were made using the program *ABSCOR* with max. and min. transmission factors of 0.43255 and 0.31254. The atomic scattering factors and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). The systematic absences for *hkl*: $h + k + l \neq 2n$ leading to the eight possible space groups $I4$, $I\bar{4}$, $I4/m$, $I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$ and $I4/mmm$. The structure was first solved in space group $I4mm$ using the *MULTAN*80 (Main *et al.*, 1980) program; however, during the refinement it was found that the structure can be described in space group $I4/mmm$. The final refinement was based on $|F|$ values using isotropic atomic displacement parameters and the program *CRYLSQ*. There are 23 variables refined to $R = 0.076$ and $wR = 0.046$ [$w = 1/\sigma^2(|F_{rel}|)$, $S = 5.29$] considering 607 contributing reflections. The max. shift/e.s.d. in the last cycle is 0.0008.* Final residual electron density −6.1–6.5 e Å^{-3}. The atomic positional and displacement parameters of $Sc_7Re_{4-x}Si_{10+x}$ ($x = 0.65$) are given in Table 1. Interatomic distances up to 3.5 Å are given in Table 2.

The programs used to refine the structure are all from the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The $Sc_7Re_{4-x}Si_{10+x}$ structure can be considered as a ternary substitution variant of the $Ho_{11}Ge_{10}$ type (Smith, Johnson & Tharp, 1967). The three Sc sites and the 16-fold $X(1)$ site, essentially occupied by Re atoms, correspond to the Ho sites and the four Si and the 8-fold $X(2)$ sites, essentially occupied by Si atoms, to the Ge sites in $Ho_{11}Ge_{10}$. A ternary substitution variant of $Ho_{11}Ge_{10}$ type has already been reported for $Sc_7Cr_{4+x}Si_{10-x}$ ($x = 0.8$) (Kotur, Bodak & Zavodnik, 1985); however, the $X(1)$ site is here fully

*A list of structure factors, arranged in a standard crystallographic data file (Brown, 1985), has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44526 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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occupied by Cr atoms and the $X(2)$ site by a $Cr_{0.4}Si_{0.6}$ mixture.

The $Sc_7Re_{4-x}Si_{10+x}$ structure can be built up of segments cut from the tetragonal $Zr_4Co_4Ge_7$ type, determined by Jeitschko (1969), as demonstrated in Figs. 1 and 2. In Fig. 1 is shown a projection of the $Sc_7Re_{4-x}Si_{10+x}$ structure along the [010] direction. The full or dashed circles indicate two kinds of structure segments which are separated by monoatomic layers of black Si atoms. The lower segment drawn with full

Table 1. *Atomic positional and displacement parameters for* $Sc_7Re_{4-x}Si_{10+x}$ ($x = 0{\cdot}65$) *with space group* $I4/mmm$

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

		x	y	z	U(Å^2 × 1000)
Sc(1)	16(n)	0	0·2533 (3)	0·3143 (2)	0·59 (8)
$X(1)$	16(n)	0	0·33269 (9)	0·10682 (7)	*
Si(1)	16(m)	0·2072 (4)	0·2072 (4)	0·1723 (4)	1·3 (1)
Si(2)	8(j)	0·1269 (7)	½	0	0·9 (2)
$X(2)$	8(h)	0·1085 (4)	0·1085 (4)	0	†
Sc(2)	8(h)	0·3150 (3)	0·3150 (3)	0	1·3 (1)
Sc(3)	4(e)	0	0	0·1661 (6)	1·5 (2)
Si(3)	4(e)	0	0	0·3987 (8)	0·7 (2)
Si(4)	4(d)	0	½	¼	1·2 (2)

Site occupancy: $X(1) = 81$ (1)% Re + 19% Si; $X(2) = 94{\cdot}7$ (5)% Si + 5·3% Re.

* For $X(1)$: $U_{Re} = 1{\cdot}32$ (3) Å^2 and $U_{Si} = U_{Si(1)}$.
† For $X(2)$: $U_{Re} = U_{Re}$ in $X(1)$ and $U_{Si} = U_{Si(1)}$.

Table 2. *Interatomic distances up to* 3·5 Å *in* $Sc_7Re_{4-x}Si_{10+x}$

Sc(1)– Si(4)	2·589 (3)	$X(2)$–2$X(2)$	2·129 (4)
Si(3)	2·761 (6)	2Sc(3)	2·808 (7)
Si(2)	2·899 (5)	2Si(1)	2·815 (5)
2Si(1)	2·906 (4)	Sc(2)	2·866 (2)
2Si(1)	2·906 (6)	4X(1)	2·8806 (9)
X(1)	3·063 (4)	$X(2)$	3·0109 (1)
2X(1)	3·134 (3)		
Sc(3)	3·264 (7)	Si(1)– Si(1)	2·516 (7)
2Sc(2)	3·281 (4)	2X(1)	2·554 (4)
		$X(2)$	2·815 (5)
Sc(2)–2Si(2)	2·589 (6)	Sc(3)	2·877 (3)
$X(2)$	2·866 (2)	Sc(2)	2·879 (5)
2Si(1)	2·879 (5)	2Sc(1)	2·906 (4)
2Si(3)	2·946 (6)	2Sc(1)	2·906 (6)
4Sc(1)	3·281 (4)		
4X(1)	3·451 (3)	Si(2)– Si(2)	2·49 (1)
		4X(1)	2·563 (4)
Sc(3)–4X(2)	2·808 (7)	2Sc(2)	2·589 (6)
4Si(1)	2·877 (3)	2Sc(1)	2·899 (5)
4Sc(1)	3·264 (7)		
Si(3)	3·32 (1)	Si(3)–4Sc(1)	2·761 (6)
4X(1)	3·372 (2)	Si(3)	2·89 (2)
		4Sc(2)	2·946 (6)
X(1)–2Si(1)	2·554 (4)	Sc(3)	3·32 (1)
2Si(2)	2·563 (4)		
Si(4)	2·621 (1)	Si(4)–4Sc(1)	2·589 (3)
2X(2)	2·8806 (9)	4X(1)	2·621 (1)
X(1)	3·050 (1)		
Sc(1)	3·063 (4)		
2Sc(1)	3·134 (3)	$X(1) = Re_{0.81}Si_{0.19}$	
X(1)	3·2834 (9)	$X(2) = Re_{0.053}Si_{0.947}$	
Sc(3)	3·372 (2)		
2Sc(2)	3·451 (3)		

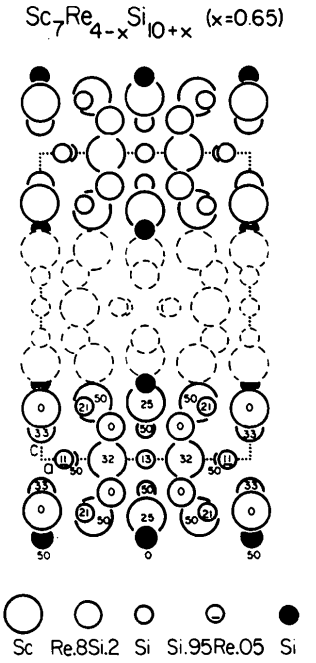

Fig. 1. Projection of $Sc_7Re_4Si_{10}$ along [010]. The values inscribed in the circles (or close to the circles) correspond to $\pm 100y$. Thus there are always two atoms superimposed except when $y = 0$. The slab of atoms drawn with full circles corresponds to a segment of the $Zr_4Co_4Ge_7$ structure. The slab of atoms drawn with dashed circles is identical to the first but displaced by ½ ½ ½. Between the slabs are monoatomic layers of black Si atoms.

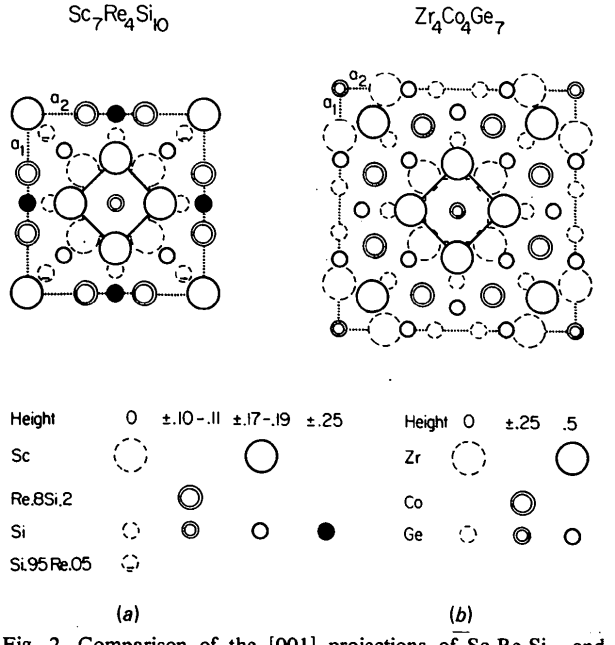

Fig. 2. Comparison of the [001] projections of $Sc_7Re_4Si_{10}$ and $Zr_4Co_4Ge_7$. (*a*) Projection of half a unit cell of $Sc_7Re_4Si_{10}$ ($-0{\cdot}25 \le z \le +0{\cdot}25$) corresponding to the slab drawn with full circles and black circles in Fig. 1. (*b*) Projection of one unit cell of $Zr_4Co_4Ge_7$ ($-0{\cdot}5 \le z \le +0{\cdot}5$).

circles is identical to the upper one but displaced by $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The lower structure slab in Fig. 1 is shown in Fig. 2(*a*) in a projection along [001]. A comparison with Fig. 2(*b*) demonstrates that the $Sc_7Re_{4-x}Si_{10+x}$ slab, except for the black Si atoms at the top of the slab, corresponds, atom for atom, to the central part of the tetragonal $Zr_4Co_4Ge_7$ structure [$0{\cdot}14 \le x(Zr_4Co_4Ge_7) \le 0{\cdot}86$ and $0{\cdot}14 \le y(Zr_4Co_4Ge_7) \le 0{\cdot}86$]. In the $Zr_4Co_4Ge_7$ structure parallel *infinite* rectilinear columns (perpendicular to the plane of projection) of Ge-centred square antiprisms are formed, while in the case of $Sc_7Re_{4-x}Si_{10+x}$ the columns of the Si-centred antiprisms are *finite*. Note that $c(Zr_4Co_4Ge_7)$ is somewhat less than $\frac{1}{2}c(Sc_7Re_{4-x}Si_{10+x})$ because of the presence of the extra layer of Si atoms in the $Sc_7Re_{4-x}Si_{10+x}$ structure.

In the same way as segments of the $Zr_4Co_4Ge_7$ structure can be used to construct slabs of the $Sc_7Re_4Si_{10}$ structure it is possible to use segments of the $Sc_7Re_4Si_{10}$ structure to construct the tetragonal $YbMo_2Al_4$ structure, determined by Fornasini & Palenzona (1976). In Fig. 3(*b*) is shown the slab of $Sc_7Re_4Si_{10}$, already presented in Fig. 2(*a*), but now shifted to have the origin at the centre of the drawing. The central part of the $Sc_7Re_4Si_{10}$ slab [$-\frac{1}{3} \le x(Sc_7Re_4Si_{10}) \le +\frac{1}{3}$ and $-\frac{1}{3} \le y(Sc_7Re_4Si_{10}) \le +\frac{1}{3}$] corresponds, atom for atom, to one unit cell of the $YbMo_2Al_4$ structure, presented in Fig. 3(*a*). The $YbMo_2Al_4$ structure was shown before by Parthé & Chabot (1984) to be a checker-board arrangement of intergrowth columns of the $CeMg_2Si_2$ type (Zmii & Gladyshevskii, 1971).

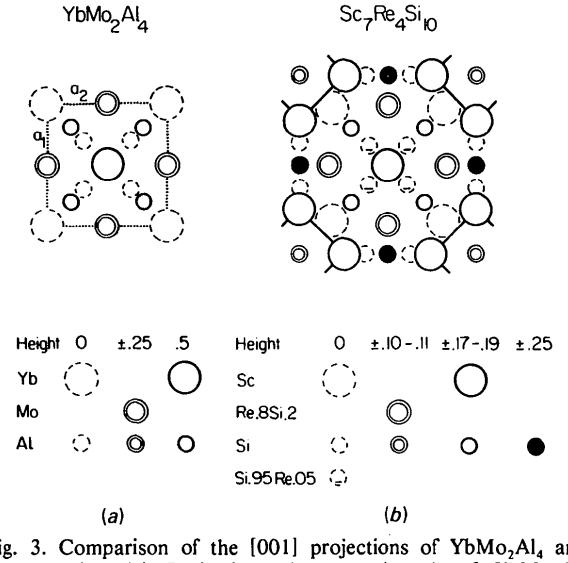

Fig. 3. Comparison of the [001] projections of $YbMo_2Al_4$ and $Sc_7Re_4Si_{10}$. (*a*) Projection of one unit cell of $YbMo_2Al_4$ ($-0{\cdot}5 \le z \le +0{\cdot}5$). (*b*) Projection of half a unit cell of $Sc_7Re_4Si_{10}$ ($-0{\cdot}5 \le x,y \le +0{\cdot}5$ and $-0{\cdot}25 \le z \le +0{\cdot}25$).

From Fig. 3(*b*) we can see that instead of forming dumbbells which had been found for example in $TiMnSi_2$ (Steinmetz, Venturini, Roques, Engel, Chabot & Parthé, 1982), V_7Al_{45} (Brown, 1959), $ZrFeSi_2$ (Yarmolyuk, Kotur & Grin', 1980) and $Zr_4Co_4Ge_7$ (Jeitschko, 1969), the four $X(2)$ atoms (the marked dashed circles) around the centre of the drawing form a very tightly bound square in the xy plane. The distances between the neighbouring atoms are 2·129 Å which is 19·3% smaller than the sum of the metallic radii of the Si atoms. This square is in the centre of a 22-atom coordination figure formed by the interpenetration of four deformed 12-atom Frank–Kasper polyhedra (or icosahedra).

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