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$Sc_5T_4Si_{10}$ (T = Co, Rh, Ir) and $Y_5T_4Ge_{10}$ (T = Os, Ir) with a New Tetragonal Structure Type

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Abstract. $Sc_5Co_4Si_{10}$, $P4/mbm$, $Z = 2$, $a = 12{\cdot}01$ (1), $c = 3{\cdot}936$ (5) Å, $D_c = 4{\cdot}34$ (1), $D_o = 4{\cdot}33$ (1) Mg m^{-3}, μ(Mo $K\alpha$) = 9·7 mm^{-1}. Final $R = 0{\cdot}04$ for 419 reflections. Isostructural compounds are $Sc_5Rh_4Si_{10}$ [$a = 12{\cdot}325$ (6), $c = 4{\cdot}032$ (3) Å], $Sc_5Ir_4Si_{10}$ [$a = 12{\cdot}316$ (5), $c = 4{\cdot}076$ (3) Å], $Y_5Os_4Ge_{10}$ [$a = 13{\cdot}006$ (8), $c = 4{\cdot}297$ (5) Å] and $Y_5Ir_4Ge_{10}$ [$a = 12{\cdot}927$ (5), $c = 4{\cdot}308$ (5) Å].

Introduction. During a seach for superconductivity in rare-earth–transition-metal silicides, a series of tetragonal compounds of formula $R_5T_4X_{10}$ (R = Sc, Y, T = Co, Rh, Ir, Os, X = Si, Ge) was found (Braun, 1979). Most of them are good superconductors with critical temperatures up to 8·6 K (Braun & Segre, 1980). Their composition was determined by microprobe analysis of a sample belonging to the Sc–Rh–Si system (Braun, Burri & Rinderer, 1979). In the analogous Co system, Kotur, Bodak & Gladyshevskii (1977) reported a tetragonal phase of approximate composition $Sc_3Co_2Si_5$. To our knowledge, the structure has not been determined. In view of the space group indicated ($P4/mbm$) and the similarity of the lattice parameters ($a = 11{\cdot}99$, $c = 3{\cdot}96$ Å) their $Sc_3Co_2Si_5$ and our $Sc_5Co_4Si_{10}$ are likely to be identical.

Prior to the present study, single crystals of $Sc_5Ir_4Si_{10}$ were examined by Weissenberg and precession photographs. The Laue class $4/mmm$ and the systematic absences ($0kl$: $k = 2n + 1$) led to the possible space groups $P4bm$, $P\bar{4}b2$ or $P4/mbm$. A model was obtained by direct methods, but despite corrections for isotropic absorption and extinction, anisotropic refinement in non-centrosymmetric $P4bm$ yielded only an unsatisfactory $R = 0{\cdot}18$. Thus, it became desirable to collect a new set of data, preferably for a compound in which Ir was replaced by a lighter transition metal. A sample of $Sc_5Co_4Si_{10}$ was prepared by arc-melting and subsequently cooled slowly (6 K h^{-1}) from 1700 to 1100 K. A single crystal, isolated from the crushed sample, was mounted on a four-circle diffractometer (Philips PW 1100, Mo $K\alpha$, graphite monochromator). Integrated intensities were collected

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in the θ–2θ scan mode up to a limit of $\sin\theta/\lambda = 0{\cdot}71$ Å^{-1}. Of 425 unique reflections, 419 had $I > 3\sigma(I)$. The positional parameters of $Sc_5Ir_4Si_{10}$, with z fixed to 0 or $\frac{1}{2}$, were taken as starting values for a full-matrix least-squares refinement (34 parameters) in *P4/mbm* with *CRYLSQ* of XRAY (Stewart, 1976). Spherical absorption corrections and an isotropic correction for secondary extinction were applied and the weighting scheme for the final cycles was $w = 1/\sigma^2(F)$. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The final $R = \sum|\Delta F|/\sum|F_o|$ was 0·04.* The atomic parameters are given in Table 1, and selected bond lengths in Table 2.

Table 1. *Positional* ($\times 10^4$) *and equivalent isotropic thermal* ($\times 10^2$) *parameters for* $Sc_5Co_4Si_{10}$

Space group *P4/mbm* (No. 127).

E.s.d.'s in units of the least significant figure are given in parentheses.

		x	y	z	U_{eq} (Å^2)
Sc(1)	2(*a*)	0	0	0	0·86 (4)
Sc(2)	4(*h*)	1756 (1)	6756 (1)	$\frac{1}{2}$	1·06 (4)
Sc(3)	4(*h*)	3882 (1)	8882 (1)	$\frac{1}{2}$	1·18 (4)
Co	8(*i*)	2540 (1)	5240 (1)	0	0·86 (4)
Si(1)	4(*g*)	679 (1)	5679 (1)	0	0·89 (5)
Si(2)	8(*i*)	1575 (1)	1985 (1)	0	1·26 (5)
Si(3)	8(*j*)	1638 (1)	31 (1)	$\frac{1}{2}$	1·38 (5)

Table 2. *Selected bond distances* (Å) *in* $Sc_5Co_4Si_{10}$

E.s.d.'s are in parentheses.

Sc(1)–Si(2)	4 × 3·043 (2)	Si(1)–Sc(2)	2 × 2·688 (2)
Si(3)	8 × 2·783 (2)	Sc(3)	4 × 2·968 (2)
Co	4 × 2·969 (3)	Si(1)	1 × 2·305 (2)
		Co	2 × 2·297 (2)
Sc(2)–Si(2)	4 × 2·823 (2)		
Si(1)	2 × 2·688 (2)	Si(2)–Sc(1)	1 × 3·043 (2)
Si(3)	2 × 2·831 (2)	Sc(2)	2 × 2·823 (2)
Co	4 × 2·842 (2)	Sc(3)	2 × 3·060 (2)
		Si(2)	1 × 2·446 (3)
Sc(3)–Si(2)	4 × 3·060 (2)	Si(3)	2 × 2·787 (3)
Si(1)	4 × 2·968 (2)		2 × 3·064 (3)
Si(3)	2 × 3·028 (3)	Co	1 × 2·253 (2)
Co	4 × 3·074 (2)		1 × 2·350 (2)
Co–Sc(1)	1 × 2·969 (3)	Si(3)–Sc(1)	2 × 2·783 (2)
Sc(2)	2 × 2·842 (2)	Sc(2)	1 × 2·831 (2)
Sc(3)	2 × 3·074 (2)	Sc(3)	1 × 3·028 (3)
Si(2)	1 × 2·253 (2)	Si(2)	2 × 2·787 (3)
	1 × 2·350 (2)		2 × 3·064 (3)
Si(1)	1 × 2·297 (2)	Si(3)	2 × 2·783 (3)
Si(3)	2 × 2·216 (2)	Co	2 × 2·216 (2)

The small shift of the positional parameters during the refinement confirmed the isotypy of $Sc_5Ir_4Si_{10}$ with $Sc_5Co_4Si_{10}$. The isotypy of $Sc_5Rh_4Si_{10}$, $Y_5Os_4Ge_{10}$, and $Y_5Ir_4Ge_{10}$ with $Sc_5Co_4Si_{10}$ was established by comparison of their powder-diffractometer tracings with intensities calculated with *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). The lattice parameters were calculated by least squares from about 30 diffraction lines. It should be noted, however, that single-phase samples were not obtained for the germanides under the current preparation conditions (Braun & Segre, 1980).

Discussion. A projection of the $Sc_5Co_4Si_{10}$ structure along *c* is shown in Fig. 1. The Co and Si atoms form planar nets of pentagons and hexagons which are stacked parallel to the basal plane and connected along *c via* Co—Si—Co zigzag chains. The pentagon–hexagon layers are separated by layers of Sc. All Co—Si and Si—Si distances are conspicuously short and indicative of strong covalent interactions (Table 2). Networks of Si and transition-metal atoms also occur in many other ternary rare-earth–transition-metal silicides, *e.g.* $ThCr_2Si_2$, $CeNiSi_2$, $CeRe_4Si_2$ and $LaRe_2Si_2$ (Pecharskii, Bodak & Gladyshevskii, 1977).

A different way to describe the structure is by the stacking of building blocks. As shown in Fig. 2, there are two types of blocks, both familiar from binary or ternary silicides. One is a trigonal prism formed by six Sc atoms which is centered by Si. The edges of the rectangular faces are longer than those of the trigonal faces, such that the prism can be classified as stretched ($1{\cdot}08 = h/l > 1$; Le Roy, Moreau, Paccard & Parthé, 1977). Si-centered prisms of this type are typical of many transition-metal and rare-earth silicides. In the present compound, they are stacked in $^1_\infty$ columns along *c*, as, for example, in ScSi which belongs to the CrB structure type. However, in contrast to the latter compound, the columns are not connected to give $^2_\infty$ sheets, but are broken up into columns of double

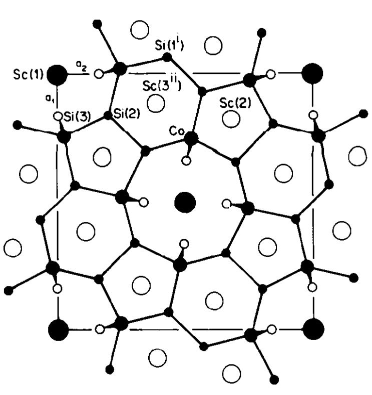

Fig. 1. Projection of the $Sc_5Co_4Si_{10}$ structure along [001]. Bonds shorter than 2·7 Å are shown by lines. Filled circles: $z = 0,1$; open circles: $z = \frac{1}{2}$. Symmetry code: (i) $-x, -y, z$; (ii) $1-y, x, z$.

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* Lists of structure factors and anisotropic thermal parameters for $Sc_5Co_4Si_{10}$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35396 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

prisms, similar to those formed by U in U_3Si_2 (Zachariasen, 1948). The Si–Si distances within the double prisms are practically the same in $Sc_5Co_4Si_{10}$ and U_3Si_2 ($d_{Si-Si} = 2{\cdot}30$ Å). They are shorter than in ScSi (2·43 Å; Schob & Parthé, 1965) and even shorter than in elemental silicon (2·35 Å).

The other structural unit is a Co-centered tetragonal antiprism $CoSc_4Si_4$ (shaded in Fig. 2). It consists of four Sc atoms forming a rectangular face of the Sc double prism and four Si atoms having a nearly square-planar configuration. A fifth Si atom, *i.e.* that at the center of the Sc prism, completes these antiprisms to give $CoSc_4Si_5$ units. TR_4Si_5 building blocks ($T =$ transition metal, $R =$ rare earth, Sc, Y, U) having this geometry are common structural elements in several ternary rare-earth–transition-metal silicides, *e.g.* $CeNiSi_2$ (Bodak & Gladyshevskii, 1970), $U_2Co_3Si_5$ (Aksel'rud, Yarmolyuk & Gladyshevskii, 1977), $ScNiSi_3$ (Kotur, Bodak, Mys'kiv & Gladyshevskii, 1977), $LaRe_2Si_2$ (Pecharskii, Bodak & Gladyshevskii, 1977) and $ScNi_2Si_3$ (Kotur, Bodak & Gladyshevskii, 1978). In the present compound, the $CoSc_4Si_5$ units are stacked in $^1_\infty$ columns parallel to c, sharing triangular faces. This arrangement leaves open channels which are occupied by the remaining Sc atoms. The Si environment of the latter represents a distorted cuboctahedron.

The existence of superconducting phases in the Sc–Co,Rh,Ir–Si systems has been pointed out previously (Braun & Segre, 1980). The elements Co and Rh are not superconducting, and Ir only at 0·1 K, whereas Sc (Wittig, Probst, Schmidt & Gschneidner, 1979) and Si (Wittig, 1966) become superconducting only under pressure. Among the binary phases, only $CoSi_2$ ($T_c = 1{\cdot}2$ K; CaF_2-type; Matthias & Hulm, 1953) and $Ir_{2.5}Sc$ ($T_c < 2{\cdot}5$ K; see Roberts, 1976) are known to be superconductors above 1 K. In fact, $Sc_5Co_4Si_{10}$ has one of the highest transition temperatures known for Co compounds ($T_c = 4{\cdot}9$ K; Braun & Segre, 1980). Thus, the magnetic character of the Co atom in this phase either is lost or does not interfere significantly with the BCS pairing. This behavior is quite unusual, especially in view of the rather even distribution of the transition-metal atoms in the structure. The absence of Co–Co contacts is in contrast to most ternary superconductors known today, where the transition metal forms clusters (Vandenberg & Matthias, 1977).

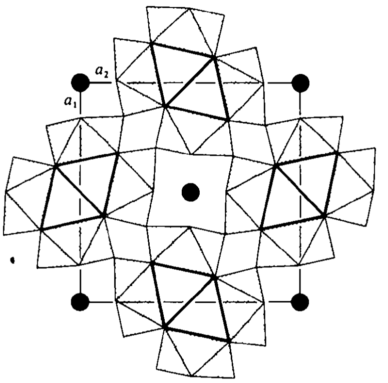

Fig. 2. Building blocks of the $Sc_5Co_4Si_{10}$ structure: Si-centered trigonal prisms (heavy lines) and distorted tetragonal antiprisms centered by Co (shaded). The filled circles represent Sc(1).

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