ERMER, O. & DUNITZ, J. (1970). *Acta Cryst.* A26, 163.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

GESI, K., OZAWA, K., OSAKA, T. & MAKITA, Y. (1980). *J. Phys. Soc. Jpn*, 49, 1083–1089.

GOSSNER, B. (1904). *Z. Kristallogr.* 38, 110–168.

HARTMAN, P. (1963). *Z. Kristallogr.* 119, 65–78.

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* 19, 1014–1018.

REDDY, A. D., SATHYANARAYAN, S. G. & SASTRY, G. S. (1982). *Solid State Commun.* 43, 937–940.

SCHOMAKER, V. & MARSH, R. E. (1979). *Acta Cryst.* B35, 1933–1934.

SUZUKI, S. & MAKITA, Y. (1978). *Acta Cryst.* B34, 732–735.

SYAMAPRASAD, U. & VALLABHAN, C. P. G. (1981). *J. Phys. C*, 14, L571–L574.

A Classification Scheme for Ternary Structures with Infinite Antiprism and Octahedron Columns used to Predict the Structure of $Sc_3Re_2Si_4$

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Abstract

A classification of ternary transition-metal silicides (and germanides) containing infinite parallel columns of Si(Ge)-centered square antiprisms and infinite parallel columns of transition-metal-centered octahedra is given which is based on the composition of the antiprisms and on the linkage of the octahedra. This scheme allows one to classify the following structure types: $Zr_4Co_4Ge_7$, $Nb_4Cr_2Si_5$, $Nb_2Cr_4Si_5$, $Hf_2Ru_3Si_4$, and also $ZrFeSi_2$, $ZrMnSi_2$ and $LuMnGe_2$. The previously reported $Sc_3Re_2Si_3$ structure has structural features which could be classified in the scheme if extra Si atoms are present. It is shown that $Sc_3Re_2Si_3$ is in fact in error, the true composition being $Sc_3Re_2Si_4$ and its structure represents the eighth structure type of this structure family. $Sc_3Re_2Si_4$: $M_r = 619.61$, monoclinic, $mC72$, $C2/c$, $a = 19.567$ (1), $b = 5.3367$ (4), $c = 13.705$ (4) Å, $\beta = 125.768$ (7)°, $V = 1161.197$ (4) Å^3, $Z = 8$, $D_x = 7.087$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 47.9$ mm^{-1}, $F(000) = 2152$, $T = 293$ K, $wR = 0.055$ for 1552 independent contributing reflections.

Introduction

In two recent systematic studies of the structures of ternary rare-earth – transition-metal silicides and homologues (Gladyshevskii & Bodak, 1982; Parthé & Chabot, 1984) it has been possible to correlate a great number of different structure types from geometric considerations. One of the aims of such an undertaking is to understand and interpret the sometimes complicated chemical formulas in relation to the structural features. In the case of ternary structures with centered trigonal prisms it was, for example, possible to formulate the so-called waist-contact-restriction rule. This rule permits the calculation of the correct composition for complete atom ordering at the prism centers for structures which were previously reported as partially ordered (Parthé, Chabot & Hovestreydt, 1983; Parthé & Hovestreydt, 1985).

In this paper we draw attention to particular ternary structures of general composition $R_xT_yM_z$ where $R =$ very late rare-earth element, Sc or a transition element of the fourth group (also sometimes Nb or Ta); $T =$ smaller transition element of Cr, Mn, Fe or Co group (also V); and $M =$ Si or Ge. The structures of interest here are characterized by two kinds of infinite columns, both of which are parallel to the shortest cell axis (of about 5 to 6 Å). One is formed of face-shared square antiprisms of R atoms or a mixture of R and T atoms, each antiprism being centered by an M atom. The second kind of infinite column consists of face-shared octahedra of M atoms, each octahedron being centered by a T atom. The centered antiprisms and centered octahedra may occasionally be deformed, but any distance between the central atom and an atom forming the polyhedron is always equal to or smaller than the sum of the metallic radii (Teatum, Gschneidner & Waber, 1960).

It was of interest to find a classification scheme for structures presenting these two kinds of columns in order to predict compositions of new structures with similar features.

Classification according to composition of antiprism columns and linkage of octahedron columns

Eight ordered structure types are known with the structural features discussed above. These types are found with more than 40 different $R_xT_yM_z$ compounds. A list of compounds crystallizing with these structures is given in Table 1. Drawings of the structure types, in a projection along the column axes, can be found in Fig. 1.

The structures can be conveniently classified according to:

- the nature of the atoms forming the square antiprism columns and
- the linkage of the octahedron columns.

Nature of the atoms forming the antiprism columns

Experimentally, it is found that the M-centered antiprisms can be formed either of R atoms only (R_8M), of R and T atoms in the ratio $3:1$ (R_6T_2M) or, finally, of equal amounts of R and T atoms (R_4T_4M). The antiprisms are face-shared to form infinite columns. The segments of the infinite columns within the height of one unit cell have the corresponding compositions: R_8M_2, $R_6T_2M_2$ and $R_4T_4M_2$. These three formulas are given on the top row of Fig. 1.
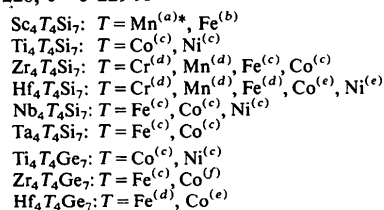
Linkage of the octahedron columns

The octahedra are always formed by the M atoms and are always centered by T atoms (M_6T). They share faces and form infinite columns. The segment of an octahedron column within the height of one unit cell has the composition M_6T_2. The infinite octahedron columns need not be isolated, but can be edge-shared with neighboring octahedron columns. If each octahedron column is edge-shared with two others the unit-cell segment of each column has the composition $M_2M_{4/2}T_2 = M_4T_2$. If it is edge-shared with three others the composition is then $M_{6/2}T_2 \equiv M_3T_2$. These three formulas are written in the first column on the left-hand side of Fig. 1.

Composition of ternary compounds

To obtain the formulas given in the central part of Fig. 1, one has simply to add to the formula for a particular antiprism column the formula for a particular octahedron column. Attention has to be paid, however, that the ratio of the number of octahedron columns to the number of antiprism columns varies from $1:1$ to $2:1$ to $4:1$ depending on the mutual linkage of the octahedron columns (edge links with no, two or three neighboring parallel octahedron columns). In this way, one can obtain the compositions of $Zr_4Co_4Ge_7$, $Nb_4Cr_2Si_5$, $Nb_2Cr_4Si_5$, $Hf_2Ru_3Si_4$ and $Sc_3Re_2Si_4$, the last being a new type of this structure family to be discussed in detail below. More

Table 1. *List of seven ordered structure types, and their isotypes, all characterized by infinite columns of face-shared Si- or Ge-centered antiprisms and infinite columns of face-shared T-centered Si or Ge octahedra*
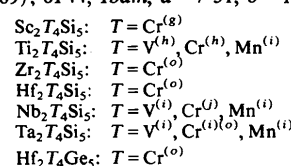
$Zr_4Co_4Ge_7$ V-phase type (Jeitschko, 1969); $tI60$, $I4/mmm$, $a = 13·228$, $c = 5·229$ Å

$Sc_4T_4Si_7$: $T = Mn^{(a)*}$, $Fe^{(b)}$
$Ti_4T_4Si_7$: $T = Co^{(c)}$, $Ni^{(c)}$
$Zr_4T_4Si_7$: $T = Cr^{(d)}$, $Mn^{(d)}$, $Fe^{(c)}$, $Co^{(c)}$
$Hf_4T_4Si_7$: $T = Cr^{(d)}$, $Mn^{(d)}$, $Fe^{(d)}$, $Co^{(e)}$, $Ni^{(e)}$
$Nb_4T_4Si_7$: $T = Fe^{(c)}$, $Co^{(c)}$, $Ni^{(c)}$
$Ta_4T_4Si_7$: $T = Fe^{(c)}$, $Co^{(c)}$
$Ti_4T_4Ge_7$: $T = Co^{(c)}$, $Ni^{(c)}$
$Zr_4T_4Ge_7$: $T = Fe^{(c)}$, $Co^{(f)}$
$Hf_4T_4Ge_7$: $T = Fe^{(d)}$, $Co^{(e)}$

$Nb_4Cr_2Si_5$ type (Steinmetz & Roques, 1977); $oI44$, $Ibam$, $a = 7·800$, $b = 16·32$, $c = 5·017$ Å†

$Ti_4T_2Si_5$: $T = V^{(h)}$, $Cr^{(h)}$
$Nb_4T_2Si_5$: $T = V^{(i)}$, $Cr^{(i)}$
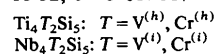
$Nb_2Cr_4Si_5$ type (Kripyakevich, Yarmolyuk & Gladyshevskii, 1969); $oI44$, $Ibam$, $a = 7·51$, $b = 15·83$, $c = 4·92$ Å

$Sc_2T_4Si_5$: $T = Cr^{(g)}$
$Ti_2T_4Si_5$: $T = V^{(h)}$, $Cr^{(h)}$, $Mn^{(i)}$
$Zr_2T_4Si_5$: $T = Cr^{(o)}$
$Hf_2T_4Si_5$: $T = Cr^{(o)}$
$Nb_2T_4Si_5$: $T = V^{(i)}$, $Cr^{(j)}$, $Mn^{(i)}$
$Ta_2T_4Si_5$: $T = V^{(i)}$, $Cr^{(i)(o)}$, $Mn^{(i)}$
$Hf_2T_4Ge_5$: $T = Cr^{(o)}$
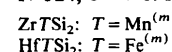
$Hf_2Ru_3Si_4$ type (Chabot, Parthé & Braun, 1985); $mC72$, $C2/c$, $a = 18·949$, $b = 5·3252$, $c = 13·227$ Å, $\beta = 127·61°$

$Zr_2T_3Si_4$: $T = Ru^{(k)}$
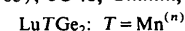$Hf_2T_3Si_4$: $T = Ru^{(k)}$
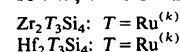
$ZrFeSi_2$ type (Yarmolyuk, Kotur & Grin, 1980); $oC96$, $Cmca$, $a = 5·16$, $b = 19·02$, $c = 14·29$ Å

$ScTSi_2$: $T = Fe^{(l)}$‡
$ZrTSi_2$: $T = Fe^{(l)}$
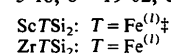
$ZrMnSi_2$ type (Venturini, Steinmetz & Roques, 1982); $oI48$, $Immm$, $a = 17·324$, $b = 7·8918$, $c = 5·166$ Å

$ZrTSi_2$: $T = Mn^{(m)}$
$HfTSi_2$: $T = Fe^{(m)}$

$LuMnGe_2$ type (Meyer, Venturini, Malaman, Steinmetz & Roques, 1983); $oC48$, $Cmmm$, $a = 5·466$, $b = 18·519$, $c = 8·173$ Å

$LuTGe_2$: $T = Mn^{(n)}$

References: (a) Kotur, Bodak & Kotur (1980). (b) B. Chabot; cited in Parthé & Chabot (1984). (c) Jeitschko, Jordan & Beck (1969). (d) Lysenko & Yarmolyuk (1974). (e) Markiv, Gladyshevskii, Skolozdra & Kripyakevich (1967). (f) Jeitschko (1969). (g) Kotur & Sikiritsa (1982). (h) Hallais (1971). (i) Steinmetz & Roques (1977). (j) Kripyakevich, Yarmolyuk & Gladyshevskii (1969). (k) Chabot, Parthé & Braun (1985). (l) Yarmolyuk, Kotur & Grin (1980). (m) Venturini, Steinmetz & Roques (1982). (n) Meyer, Venturini, Malaman, Steinmetz & Roques (1983). (o) Lysenko, Yarmolyuk & Paranchuk (1975).

* In the publication, the Wyckoff position of Si(2) is incorrectly given as $8(j)$ instead of $8(i)$.

† The a and b axes have been interchanged (which is possible without changing the space-group setting) in order to facilitate the comparison with the $Nb_2Cr_4Si_5$ type.

‡ A second modification exists with $TiMnSi_2$ type.

stoichiometries have been obtained as shown in Fig. 1 and for which no examples are known as yet. In fact, the composition for $Sc_3Re_2Si_4$ was deduced from

this classification scheme as will be shown below. As can be verified by a study of the drawings in Fig. 1, the observed structural features are as postulated. The $Nb_4Cr_2Si_5$ and $Nb_2Cr_4Si_5$ as well as the $Sc_3Re_2Si_4$ and the $Hf_2Ru_3Si_4$ types are substitution variants. In $Hf_2Ru_3Si_4$ and $Sc_3Re_2Si_4$, in distinction to the other structure types listed in Fig. 1, some of the columns are displaced with respect to each other by $\frac{1}{4}$ of the height of one unit cell (see later discussion of $Sc_3Re_2Si_4$). The octahedron columns in the two structures are, however, isolated, and that is in agreement with the classification scheme.

Presence of extra M atoms between the antiprism columns

The $ZrFeSi_2$, $ZrMnSi_2$ and $LuMnGe_2$ structures all have $R_6T_2M_2$ antiprism columns and two-edge-shared M_4T_2 octahedron columns. There are twice as many octahedron columns as antiprism columns. The expected composition is here $2M_2M_{4/2}T_2 + R_6T_2M_2 \equiv R_3T_3M_5$. We note, however, that there are extra M atoms between the antiprism columns leading to the corrected formula $R_3T_3M_5 + M \equiv RTM_2$. These extra M atoms ensure that also the T

atoms which participate in the formation of the anti-prisms are octahedrally surrounded by M atoms.

Other structures related to this structure family

The $TiMnSi_2$ structure ($oP48$, $Pbam$) (Steinmetz, Venturini, Roques, Engel, Chabot & Parthé, 1982), also found with $ZrCrSi_2$ (Yarmolyuk, Sikiritsa, Akselrud, Lysenko & Gladyshevskii, 1982), contains Si-centered antiprism columns and T-centered Si octahedron columns, where both kinds of columns are finite in length. Octahedron columns and square-antiprism columns are respectively formed by three and four polyhedra only. For details see Fig. 1 in Steinmetz et al. (1982).

Another related structure type is $HfFe_6Ge_6$ ($hP13$, $P6/mmm$) (Olenitch, Akselrud & Yarmolyuk, 1981), reported also with $LuFe_6Ge_6$ (Chabot & Parthé, 1983). In this structure one finds infinite columns of Fe-centered face-shared Ge octahedra but no M-centered antiprism columns. Each octahedron column is two-edge linked with two neighboring octahedron columns. In this way, planar octahedron sheets are formed as in $LuMnGe_2$ (middle part of Fig. 1); however, as seen in Fig. 2, these structural
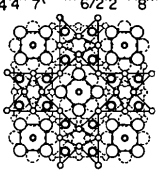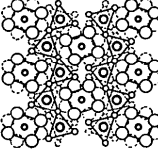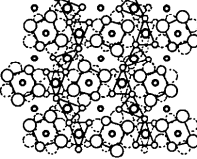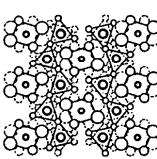
Compositions of infinite M centered antiprism columns

Fig. 1. Eight structure types with infinite antiprism columns and infinite octahedron columns classified according to composition of the M-centered antiprism columns and the linkage of T-centered octahedron columns. The outlines of the unit cells have been omitted on purpose to enhance the clarity of the drawings. Large circles: R atoms, medium circles: T atoms, small circles: M atoms. Fully drawn circles: height $\frac{1}{2}$, dashed circles: height 0, bold circles: height $\frac{1}{4}$ and $\frac{3}{4}$. For the height of the atoms in $Sc_3Re_2Si_4$ and $Hf_2Ru_3Si_4$, see legend of Fig. 3 [the shift by $\pm\frac{1}{8}$ does not apply to the Si(3) atom].

sheets are intergrown in $HfFe_6Ge_6$ by common octahedron vertices and a three-dimensional framework is formed. In the interstices of the framework are found other Fe atoms (which are octahedrally surrounded by Ge atoms) and Hf atoms centering larger cavities. In fact, due to the hexagonal symmetry, equivalent intersecting octahedron columns perpendicular to the c axis, and forming angles of 60° between them, can also be considered. These octahedron columns form together a compact, hexagonal net of face-shared centered deformed octahedra.

The unsatisfactory structure proposal for $Sc_3Re_2Si_3$

Pecharskii, Bodak & Gladyshevskii (1979) made a structure proposal for $Sc_3Re_2Si_3$ (space group $B2$ with eight formula units per unit cell, $a = 19\cdot604$, $b = 13\cdot741$, $c = 5\cdot339$ Å, $\gamma = 125\cdot92°$) which they refined to an R value of $0\cdot09$. This structure [see Fig. 6(a) in Pecharskii et al., 1979] contains, parallel to the short axis, infinite Si-centered square-antiprism columns of the kind $R_6T_2M_2$ ($Sc_6Re_2Si_2$). The arrangement of the Re atoms present between the antiprism columns could not, however, be readily explained, unless it were assumed that eight Si atoms were missing in the unit cell. Were they to be inserted in the proper places they would complete the un-explained Re-atom arrangement to make an isolated infinite column of face-shared Re-centered Si octahedra. The composition would then become $Sc_3Re_2Si_4$ and the structural features would agree well with those postulated in the classification scheme for a compound $R_3T_2M_4$.

Independent of the question as to whether there are Si atoms missing, there also remains the problem whether the structure is really noncentrosymmetric.
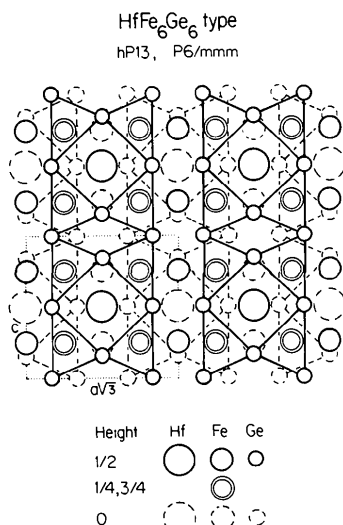

$HfFe_6Ge_6$ type

hP13, P6/mmm

Height   Hf   Fe   Ge
1/2   ◯   ◎   ○
1/4,3/4   ◎
0

Fig. 2. The hexagonal $HfFe_6Ge_6$ structure type in a projection on $(11\bar{2}0)$. The slabs of two edge-linked infinite columns of centered octahedra, as found in $LuMnGe_2$, are emphasized.

Table 2. Atomic coordinates for $Sc_3Re_2Si_4$ with space group $C2/c$

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

		x	y	z	$100U(\text{Å}^2)$
Re(1)	8(f)	0·02512 (6)	0·1157 (2)	0·42167 (9)	0·18 (2)
Si(1)	8(f)	0·1144 (5)	0·118 (2)	0·1226 (6)	0·6 (1)
Sc(1)	8(f)	0·1631 (3)	0·1261 (10)	0·3593 (4)	0·49 (9)
Re(2)	8(f)	0·23636 (6)	0·4100 (2)	0·21745 (9)	0·16 (2)
Si(2)	8(f)	0·2731 (4)	0·123 (2)	0·1114 (6)	0·5 (1)
Si(3)	8(f)	0·3261 (5)	0·273 (1)	0·4288 (7)	0·4 (1)
Sc(3)	8(f)	0·3815 (3)	0·1306 (8)	0·0497 (4)	−0·15 (8)
Sc(2)	8(f)	0·4207 (3)	0·1185 (11)	0·3459 (4)	0·65 (9)
Si(4)	4(e)	0	0·367 (3)	$\frac{1}{4}$	0·6 (3)
Si(5)	4(e)	0	0·882 (3)	$\frac{1}{4}$	0·6 (2)

After shifting the origin by $0, \frac{1}{4}, \sim 0\cdot89$ (referred to space-group setting $B2$) one finds for all atoms at sites x, y, z corresponding atoms at $-x, -y, -z$ (within or close to the limits of error). This indicates the probable presence of a symmetry center which would require a different space group for the crystallographic description of this structure.

It is for these reasons that we undertook an experimental study to verify the existence of the ternary compound $Sc_3Re_2Si_4$ and to determine its crystal structure.

Preparation and structure determination of $Sc_3Re_2Si_4$

Compound of nominal composition $Sc_3Re_2Si_4$ from Sc (99·99%), Re (99·99%) and Si (99·999%), prepared by arc-melting technique under argon atmosphere; wrapped in Ta foil and annealed for a week in a quartz tube under argon atmosphere at 1070 K. Irregular-shaped crystal with mean diameter 58 μm isolated from the crushed sample. Automatic four-circle diffractometer (Philips PW 1100), Laue symmetry $2/m$, lattice parameters given in the Abstract from 21 averaged reflections–antireflections with $40° < 2\theta < 57°$ and using Mo $K\alpha_1$. Data collection: $(\sin \theta)/\lambda < 0\cdot71$ Å^{-1}, spherical absorption correction ($3\cdot37 <$ s.a.c. $< 3\cdot61$), 3400 independent Friedel pairs measured, 1700 unique reflections ($R_{int} = 0\cdot047$), 1552 contributing reflections [1348 with $|F| > 3\sigma(F)$ and 204 less-thans calc. > obs.], systematic absences hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$, $h = 2n + 1$ and $0k0$: $k = 2n + 1$. The structure refined satisfactorily in space group $C2/c$ using, as starting point, atom positions derived from the structure proposal for $Sc_3Re_2Si_3$ (Pecharskii, Bodak & Gladyshevskii, 1979) and adding eight extra Si atoms [Si(3)]. The new Si-atom position was chosen such that, together with the other Si and Re atoms, an infinite Si_6Re_2 octahedron column is formed in analogy to the Si_6Ru_2 octahedron column in $Hf_2Ru_3Si_4$ (Chabot, Parthé & Braun, 1985). Full-matrix least squares using $|F|$ values. 37 parameters refined: one scale factor, 36 positional and isotropic thermal parameters. $R = 0\cdot078$, $wR = 0\cdot055$, $S = 2\cdot058$, $w = 1/\sigma^2(F)$, final max. $\Delta/\sigma < 10^{-4}$, final

Table 3. *Interatomic distances d (less than 3·5 Å) and rounded values* $\Delta = [100(d - \sum r)/\sum r]\%$ *for* $Sc_3Re_2Si_4$; *e.s.d.'s are given in parentheses; the atomic radii r used for* Sc, Re *and* Si *are* 1·641, 1·375 *and* 1·319 Å *respectively* (*Teatum, Gschneidner & Waber*, 1960)

	d(Å)	Δ%		d(Å)	Δ%		d(Å)	Δ%		d(Å)	Δ%
Sc(1)–1Si(1)	2·797(12)	−5·5	Sc(2)–1Si(2)	2·796(15)	−5·5	Sc(3)–1Si(3)	2·544(9)	−14·1	Re(1)–1Si(1)	2·425(10)	−10·0
1Si(3)	2·836(13)	−4·2	1Si(3)	2·805(14)	−5·2	1Si(5)	2·696(12)	−8·9	1Si(5)	2·446(7)	−9·2
1Si(3)	2·853(12)	−3·6	1Si(3)	2·850(11)	−3·7	1Si(2)	2·704(13)	−8·6	1Si(3)	2·460(12)	−8·7
1Si(2)	2·855(10)	−3·5	1Si(1)	2·851(11)	−3·7	1Si(4)	2·730(12)	−7·8	1Si(4)	2·494(6)	−7·4
1Si(2)	2·890(10)	−2·4	1Re(2)	2·884(7)	−4·4	1Si(1)	2·756(11)	−6·9	1Si(1)	2·563(10)	−4·9
1Si(4)	2·914(10)	−1·6	1Si(4)	2·885(9)	−2·5	1Si(2)	2·821(12)	−4·7	1Sc(2)	3·056(8)	+1·3
1Si(5)	2·922(10)	−1·3	1Si(5)	2·915(10)	−1·5	1Re(2)	2·983(12)	−1·1	1Sc(3)	3·058(5)	+1·4
1Re(2)	2·954(8)	−2·1	1Re(1)	3·056(7)	+1·3	1Re(1)	3·058(5)	+1·4	1Re(1)	3·093(3)	+12·5
1Si(2)	3·104(13)	+4·9	1Re(1)	3·133(7)	+3·9	1Re(1)	3·194(5)	+5·9	1Sc(2)	3·133(7)	+3·9
1Sc(3)	3·253(8)	−0·9	1Re(1)	3·158(6)	+4·7	1Sc(2)	3·249(10)	−1·0	1Sc(2)	3·158(7)	+4·7
1Re(1)	3·274(8)	+8·6	1Sc(3)	3·249(10)	−1·0	1Sc(1)	3·253(8)	−0·9	1Sc(3)	3·194(5)	+5·9
1Sc(3)	3·292(8)	+0·3	1Re(2)	3·333(9)	+10·5	1Sc(1)	3·292(8)	+0·3	1Sc(1)	3·274(8)	+8·6
1Re(2)	3·375(8)	+11·9	1Sc(1)	3·480(9)	+6·0	1Si(3)	3·454(9)	+16·7	1Sc(1)	3·438(17)	+14·0
1Re(1)	3·438(17)	+14·0									
1Sc(2)	3·480(9)	+6·0									
Re(2)–1Si(3)	2·462(11)	−8·6	Si(1)–1Re(1)	2·425(10)	−10·0	Si(2)–1Re(2)	2·491(10)	−7·5	Si(3)–1Re(1)	2·460(12)	−8·7
1Si(1)	2·487(9)	−7·7	1Re(2)	2·487(9)	−7·7	1Si(3)	2·509(12)	−4·9	1Re(2)	2·462(11)	−8·6
1Si(2)	2·491(10)	−7·5	1Si(3)	2·490(13)	−5·6	1Sc(3)	2·704(13)	−8·6	1Si(1)	2·490(13)	−5·6
1Si(3)	2·532(8)	−6·0	1Re(1)	2·563(10)	−4·9	1Re(2)	2·708(10)	+0·5	1Si(2)	2·509(12)	−4·9
1Si(1)	2·662(12)	−1·2	1Re(2)	2·662(12)	−1·2	1Sc(2)	2·796(15)	−5·5	1Re(2)	2·532(8)	−6·0
1Si(2)	2·708(10)	+0·5	1Sc(3)	2·756(11)	−6·9	1Sc(3)	2·821(12)	−4·7	1Sc(3)	2·544(9)	−14·1
2Re(2)	2·765(2)	+0·5	1Sc(1)	2·797(11)	−5·5	1Sc(1)	2·855(10)	−3·5	1Sc(2)	2·805(14)	−5·2
1Sc(2)	2·884(7)	−4·4	1Sc(2)	2·850(11)	−3·7	1Sc(1)	2·890(10)	−2·4	1Sc(1)	2·836(13)	−4·2
1Sc(1)	2·954(8)	−2·1	1Sc(2)	2·851(11)	−3·7	1Si(2)	2·960(13)	+12·2	1Sc(1)	2·853(12)	−3·6
1Sc(3)	2·983(12)	−1·1	1Si(2)	3·199(14)	+21·3	1Sc(1)	3·105(13)	+4·9	1Sc(3)	3·455(9)	+16·7
1Sc(2)	3·333(9)	+10·5				1Si(1)	3·199(14)	+21·3			
1Sc(1)	3·375(8)	+11·9									
Si(4)–2Re(1)	2·494(6)	−7·4	Si(4)–1Si(5)	2·749(16)	+4·2	Si(5)–2Re(1)	2·446(7)	−9·2	Si(5)–1Si(4)	2·749(16)	+4·2
1Si(5)	2·588(16)	−1·9	2Sc(2)	2·885(9)	−2·5	1Si(4)	2·588(16)	−1·9	2Sc(2)	2·915(10)	−1·5
2Sc(3)	2·730(12)	−7·8	2Sc(1)	2·914(10)	−1·6	2Sc(4)	2·696(12)	−8·9	2Sc(1)	2·922(10)	−1·3

residual electron density $-15 < \text{r.e.d.} < 10\,e\,\text{Å}^{-3}$. A tentative refinement of $Sc_3Re_2Si_4$ in the noncentrosymmetric space group Cc did not lead to significant change in the structure parameters. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); all programs used from the *XRAY* 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic and thermal parameters are given in Table 2, interatomic distances in Table 3.*

It should be noted that the isotropic temperature factor for Sc(3) is slightly negative (see Table 2). This fact led us to check for a possible mixed occupation by Sc and Re atoms of the 8(*f*) site corresponding to Sc(3). If a total occupancy equal to unity is assumed and if the isotropic (*U*) temperature factors are fixed at 47×10^{-4} and $18 \times 10^{-4}\,\text{Å}^2$ for Sc and Re respectively, the least-squares refinement converges to a population of 0·959 (3) Sc and 0·041 Re on the 8(*f*) site with no significant change in the reliability *R* factor.

To test the occurrence and structure of the previously published $Sc_3Re_2Si_3$, a sample was prepared at this composition and annealed at 1070 K for a week. The Guinier film obtained from this sample did not match either the simulated powder pattern

generated with the published atom coordinates of $Sc_3Re_2Si_3$ or the simulated powder pattern of $Sc_3Re_2Si_4$ [*LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977)]. Thus, the compound $Sc_3Re_2Si_3$ probably does not exist or if it exists it must have a different structure.

Discussion of $Sc_3Re_2Si_4$

The $Sc_3Re_2Si_4$ structure with unit-cell parameters quite similar to those given before for $Sc_3Re_2Si_3$ is not only centrosymmetric, but has all the expected structural features which allow it to be classified within the scheme proposed above; it represents the eighth structure type of this structure family. The $Sc_3Re_2Si_4$ structure, shown in detail in Fig. 3, has the same space group ($C2/c$) as $Hf_2Ru_3Si_4$ (Chabot, Parthé & Braun, 1985) and similar lattice constants. It should be noted, however, that the β angle for $Sc_3Re_2Si_4$ (125·768°) is slightly smaller than the one found for $Hf_2Ru_3Si_4$ (127·61°). In both structure types we find Re- or Ru-centered Si octahedra which are face-shared to form isolated infinite columns. The essential difference between both types is the composition of the columns formed of face-shared Si-centered antiprisms. The column segments within the height of one unit cell have composition $R_6T_2M_2$ in $Sc_3Re_2Si_4$ but $R_4T_4M_2$ in $Hf_2Ru_3Si_4$. For each *R*, *T* and *M* site in $Hf_2Ru_3Si_4$ one finds an equivalent *R*, *T* and *M* site in $Sc_3Re_2Si_4$ except for Ru(3) and Sc(3) (*T* replaced by *R* or *vice versa*, see Fig. 3). Since $Sc_3Re_2Si_4$ and $Hf_2Ru_3Si_4$ have so many similar struc-

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* A list of the structure factors arranged in a standard crystallographic data file (Brown, 1983) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP42033 (14 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tural features we can refer for more details to the article on $Hf_2Ru_3Si_4$ and the structure discussion given therein (Chabot, Parthé & Braun, 1985).

$Sc_3Re_2Si_4$ and $Hf_2Ru_3Si_4$ differ from the other members of this structure family in two aspects. One difference is found in the shift by $\frac{1}{4}$ of the b translation for half of the octahedron and antiprism columns [see the structure projection of $Sc_3Re_2Si_4$ in Fig. 3; for $Hf_2Ru_3Si_4$ see Fig. 1 in Chabot, Parthé & Braun (1985)]. The other difference lies in the particular deformation of the octahedron columns. The sharing Si triangular faces are no longer parallel between themselves as in the other structures and this fact has the consequence that the T elements centering the octahedron column form a zigzag chain instead of a linear chain.

It is interesting to mention the existence of $Sc_2Re_3Si_4$. This compound does not crystallize with the $Hf_2Ru_3Si_4$ structure type as might be expected from the similarity of the elements and from the structural similarities between $Hf_2Ru_3Si_4$ and $Sc_3Re_2Si_4$. $Sc_2Re_3Si_4$ crystallizes in its own structure type ($tP36$, $P4_12_12$) (Pecharskii, Bodak & Gladyshevskii, 1978), a ternary derivative of the tetragonal Zr_5Ge_4 structure type. Other ternary structure types related to $Sc_2Re_3Si_4$ are the $Ce_2Sc_3Si_4$* type ($oP36$, $Pnma$), a ternary derivative of the Sm_5Ge_4 type, and the $U_2Mo_3Si_4$ type ($mP18$, $P2_1/c$). In these structures there are neither infinite octahedron nor infinite antiprism columns. The transition elements (T), however, are all surrounded by six Si atoms. For one third of the T atoms the coordination polyhedron

corresponds to a slightly deformed octahedron. All these structure types are referenced in the paper on the structure of $Hf_2Ru_3Si_4$ (Chabot, Parthé & Braun, 1985).

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* For this particular compound, Sc = T.

$Sc_3Re_2Si_4$

mC72, C2/c
$a=19.567$, $b=5.3367$, $c=13.705$ Å, $\beta=125.768°$
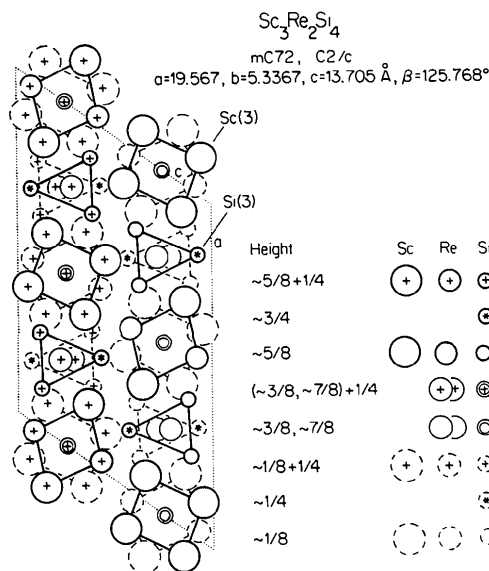

Fig. 3. The $Sc_3Re_2Si_4$ structure type in a projection along the short b axis. Infinite square antiprism columns and infinite octahedron columns parallel to [010] are indicated.

References

BROWN, I. D. (1983). *Acta Cryst.* A39, 216–224.
CHABOT, B. & PARTHÉ E. (1983). *J. Less-Common Met.* 93, L9–L11, 95, 354.
CHABOT, B., PARTHÉ, E. & BRAUN, H. F. (1985). *Acta Cryst.* C41. To be published.
GLADYSHEVSKII, E. I. & BODAK, O. I. (1982). *Crystal Chemistry of Intermetallic Compounds of the Rare Earth Metals* (in Russian). L'vov: Vishcha Shkola Publishing House.
HALLAIS, J. (1971). *Ann. Chim. (Paris)*, 6, 321–330.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JEITSCHKO, W. (1969). *Acta Cryst.* B25, 557–564.
JEITSCHKO, W., JORDAN, A. G. & BECK, P. A. (1969). *Trans. Metall. Soc. AIME*, 245, 335–339.
KOTUR, B. YA., BODAK, O. I. & KOTUR, O. YA. (1980). *Dopov. Akad. Nauk Ukr. RSR Ser. A*(8), pp. 80–83.
KOTUR, B. YA. & SIKIRITSA, M. (1982). *J. Less-Common Met.* 83, L29–L31.
KRIPYAKEVICH, P. I., YARMOLYUK, YA. P. & GLADYSHEVSKII, E. I. (1969). *Sov. Phys. Crystallogr.* 13, 677–681.
LYSENKO, L. A. & YARMOLYUK, YA. P. (1974). *2nd All-Union Conference on the Crystallochemistry of Intermetallic Compounds* (*Abstracts of Lectures*), L'vov, 3–6 October, p. 22 (in Russian).
LYSENKO, L. A., YARMOLYUK, YA P. & PARANCHUK, M. M. (1975). *Visn. L'viv. Univ. Ser. Khim.* 17, 33–35.
MARKIV, V. YA., GLADYSHEVSKII, E. I., SKOLOZDRA, R. V. & KRIPYAKEVICH, P. I. (1967). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 266–269.
MEYER, M., VENTURINI, G., MALAMAN, B., STEINMETZ, J. & ROQUES, B. (1983). *Mater. Res. Bull.* 18, 1529–1535.
OLENITCH, R. R., AKSELRUD, L. G. & YARMOLYUK, YA. P. (1981). *Dopov. Akad. Nauk Ukr. RSR Ser. A*(2), pp. 84–88.
PARTHÉ E. & CHABOT, B. (1984). In *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. GSCHNEIDNER JR & L. EYRING, Vol. 6, ch. 48, pp. 113–334. Amsterdam: North-Holland.
PARTHÉ, E., CHABOT, B. & HOVESTREYDT, E. (1983). *Acta Cryst.* B39, 596–603.
PARTHÉ, E. & HOVESTREYDT, E. (1985). *J. Less-Common Met.* In the press.
PECHARSKII, V. K., BODAK, O. I. & GLADYSHEVSKII, E. I. (1978). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, pp. 755–759.
PECHARSKII, V. K., BODAK, O. I. & GLADYSHEVSKII, E. I. (1979). *Sov. Phys. Crystallogr.* 24, 433–438.
STEINMETZ, J. & ROQUES, B. (1977). *J. Less-Common Met.* 52, 247–258.
STEINMETZ, J., VENTURINI, G., ROQUES, B., ENGEL, N., CHABOT, B. & PARTHÉ, E. (1982). *Acta Cryst.* B38, 2103–2108.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
TEATUM, E., GSCHNEIDNER, K. & WABER, J. (1960). Cited in *The Crystal Chemistry and Physics of Metals and Alloys* (1972) by W. P. PEARSON, p. 151. New York: John Wiley.

VENTURINI, G., STEINMETZ, J. & ROQUES, B. (1982). *J. Less-Common Met.* **87**, 21–30.

YARMOLYUK, YA, P., KOTUR, B. YA. & GRIN, YU. N. (1980). *Dopov. Akad. Nauk Ukr. RSR, Ser. B*(11), pp. 68–72.

YARMOLYUK, YA. P., SIKIRITSA, M., AKSELRUD, L. G., LYSENKO, L. A. & GLADYSHEVSKII, E. I. (1982). *Sov. Phys. Crystallogr.* **27**, 1090–1093.

YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

Electron-Microscopic Study of the Structure of Metastable Oxides Formed in the Initial Stage of Copper Oxidation. III. Cu₆₄O

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Abstract

Besides Cu_4O and Cu_8O reported previously, a third metastable copper oxide with the chemical composition $Cu_{64}O$ formed in the early stage of oxidation of copper has been observed by high-resolution electron microscopy. The atomic positions of Cu and O have been determined by electron diffraction and by comparison of the observed structure images with simulated ones calculated on the basis of the dynamical theory of electron diffraction and image formation theory. $Cu_{64}O$ is ordered base-centered orthorhombic with lattice constants $a = 9.74$, $b = 10.58$ and $c = 16.20$ Å. The intensity of the diffracted waves reflecting the periodicity of the O-atom arrangement in $Cu_{64}O$ is much weaker than those in Cu_4O and Cu_8O because of the lower oxygen content. Thus, the images of O atoms in the $Cu_{64}O$ crystal can only be observed at limited thicknesses. Good agreement between the observed and calculated images has been obtained, though the distance between the Cu atoms in $Cu_{64}O$ is still too small to be resolved.

1. Introduction

The contributions made by high-resolution electron microscopy (HREM) to the understanding of the early stages of copper oxidation by the present authors (Guan, Hashimoto & Yoshida, 1984; Guan, Hashimoto & Kuo, 1984) have shown that two suboxides, Cu_4O and Cu_8O, are formed as the interstitial solution of O atoms in the Cu lattice. These results strongly suggest that a series of copper suboxides containing much less oxygen than the normal ones, such as CuO and Cu_2O, might form. Suboxides in b.c.c. transition metals have been studied by several workers, but recently Dahmen & Thomas (1979) showed that previously published results claiming the $Ta_{64}C$ ordered phase are incorrect and can be explained completely in terms of oxygen contamination yielding the compound $Ta_{12}O$.

Khachaturyan (1983) has presented theoretical criteria based on elastic strain energy to predict site occupancy and ordered structures in b.c.c. transition-metal dilute solutions with C, N, O, *etc.* but similar problems concerning the interstitials in f.c.c. metals such as Cu have not been considered. In the present paper, which is the third in the series, the structure of a suboxide phase has been determined to be $Cu_{64}O$ by high-resolution structure imaging and electron diffraction.

2. Specimen preparation and observation

$Cu_{64}O$ was found in pure commercial copper powder, similarly to the case of Cu_8O. It could also be obtained by gently heating copper powder in air. Details of specimen preparation were presented in the previous paper (Guan, Hashimoto & Kuo, 1984). Electron-microscopic observations were made using a JEM 200CX electron microscope. Fig. 1 shows electron micrographs of the new suboxide of copper which, for convenience, is designated as Cu_zO. Fig. 1(*a*) is obtained from pure copper powder, while Fig. 1(*b*) is from the powder heated in air. Electron diffrac-