

We have shown that the compound with  $n = 4$  of the structure series mentioned in the *Introduction* is ordered. If we assume that all compounds of this series are ordered, that all possible prism-centre sites, which are permitted by the waist-contact restriction rule, are occupied by  $T$  atoms and all octahedral voids occupied each by one  $T$  atom, the formula of the structure series must be written as

$$R_{n^2+3n+2}T_2^{[6,o]}T_{n^2-n}^{[6,p]}M_{n^2+n}^{[6,p]}$$

which gives for  $n = 2, 3$  and  $4$  the compositions  $R_6T_2M_3$ ,  $R_5T_2M_3$  and  $R_{15}T_7M_{10}$ , respectively. We note that for  $n = 2$  and  $3$  the calculated compositions agree with those previously reported, although no complete ordering was found. Experiments are presently being undertaken to find out if these compounds are not perhaps ordered after all.

We have demonstrated here how the waist-contact restriction rule can be used to find the correct composition for perfect order of a structure, built up of centred trigonal prisms where only the structure sites are known with certainty. The predicted change from  $\text{Pr}_{15}\text{Ni}_4\text{Si}_{13}$  to  $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$  represents the second successful application of the waist-contact restriction rule, which led to the prediction of a change of composition of a ternary rare-earth-nickel silicide. From the arrangement of the centred trigonal prisms in  $\text{Ce}_{14}\text{Ni}_8\text{Si}_9$  (Mys'kiv, 1973) it was possible to conclude that the composition for perfect order should be  $\text{Ce}_{14}\text{Ni}_6\text{Si}_{11}$  (Parthé *et al.*, 1983), which was experimentally verified by Hovestreydt (1984). A further experiment is being undertaken to verify if  $\text{Ce}_{15}\text{Ni}_7\text{Si}_{10}$  also crystallizes with the ordered  $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$  type.

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## Cubic $\text{Sc}_{57}\text{Rh}_{13}$ and Orthorhombic $\text{Hf}_{54}\text{Os}_{17}$ , Two Geometrically Related Crystal Structures with Rhodium- and Osmium-Centred Icosahedra

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**Abstract.**  $\text{Sc}_{57}\text{Rh}_{13}$ :  $M_r = 3900.3$ ,  $cP140$ ,  $Pm\bar{3}$ ,  $a = 14.4051(7) \text{ \AA}$ ,  $V = 2989.1(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 4.33 \text{ g cm}^{-3}$ ,  $\text{Mo K}\alpha$ ,  $\lambda = 0.7107 \text{ \AA}$ ,  $\mu = 93.4 \text{ cm}^{-1}$ ,  $F(000) = 3564$ ,  $T = 293 \text{ K}$ ,  $wR = 0.051$  for 1013 independent reflections. Isotypic compounds are  $\text{Sc}_{57}\text{Ru}_{13}$  [ $a = 14.394(1) \text{ \AA}$ ],  $\text{Sc}_{57}\text{Ir}_{13}$  [ $a = 14.364(1) \text{ \AA}$ ] and  $\text{Sc}_{57}\text{Pt}_{13}$  [ $a = 14.415(1) \text{ \AA}$ ].  $\text{Hf}_{54}\text{Os}_{17}$ :  $M_r = 12871.9$ ,  $oI142$ ,  $Immm$ ,  $a =$

$13.856(2)$ ,  $b = 14.104(2)$ ,  $c = 14.570(2) \text{ \AA}$ ,  $V = 2847.2(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 15.0 \text{ g cm}^{-3}$ ,  $\text{Mo K}\alpha$ ,  $\lambda = 0.7107 \text{ \AA}$ ,  $\mu = 1433 \text{ cm}^{-1}$ ,  $F(000) = 10360$ ,  $T = 293 \text{ K}$ ,  $R = 0.084$  for 1057 independent reflections. The  $\text{Sc}_{57}\text{Rh}_{13}$  and  $\text{Hf}_{54}\text{Os}_{17}$  structures can be considered as slight deformations of a hypothetical cubic, body-centred structure type built up from icosahedra centred by the minority atoms. In the structural unit 12

outer icosahedra share vertices with a central one, the centres of the outer icosahedra being themselves icosahedrally arranged. Structures containing similar polyhedron units are also discussed.

**Introduction.** In the course of our structural studies on Sc-rich alloys with late transition elements two structure types have previously been identified in the Sc-rich part (>70 at. % Sc) of the phase diagrams with Group VIII elements of the second and third long period, both of them having large cubic unit cells. Sc<sub>44</sub>Os<sub>7</sub> and Sc<sub>44</sub>Ir<sub>7</sub> crystallize with the Mg<sub>44</sub>Rh<sub>7</sub> structure type, *cF408*, (Chabot, Cenziel & Parthé, 1980*b*) while the Sc<sub>11</sub>Ir<sub>4</sub> type, *cF120*, closely related to the Th<sub>6</sub>Mn<sub>23</sub> type, is also found with Sc<sub>11</sub>Ru<sub>4</sub> and Sc<sub>11</sub>Os<sub>4</sub> (Chabot, Cenziel & Parthé, 1980*a*). We want to report here on the determination of an intermediate phase, first observed by Geballe, Matthias, Compton, Corenzwit, Hull & Longinotti (1965) at the approximate composition 4:1 in the Sc–Rh and Sc–Pt systems and several years later by us in samples of composition Sc<sub>6</sub>Ru, Sc<sub>6</sub>Rh, Sc<sub>6</sub>Ir and Sc<sub>6</sub>Pt (Chabot, Cenziel & Parthé, 1980*b*). We reported a body-centred cubic cell of about 14 Å but we shall show here that the true composition of the ordered compound is Sc<sub>57</sub>T<sub>13</sub> (*T* is a transition element) and that, at thermal equilibrium, the structure has a cubic primitive cell at this composition.

As far as Zr and Hf alloys are concerned we had determined the structure of Zr<sub>11</sub>Os<sub>4</sub> to be isotypic to Sc<sub>11</sub>Ir<sub>4</sub> (Chabot, Cenziel & Parthé, 1980*a*). No such phase exists in the Hf–Os system. Waterstrat (1983) recently determined the hafnium–osmium constitution diagram and found five intermetallic phases: HfOs<sub>2</sub> (*λ* phase) with MgZn<sub>2</sub> type, *hP12*; HfOs (*δ* phase) with CsCl type, *cP2*; Hf<sub>2</sub>Os (*η* phase) with Ti<sub>2</sub>Ni type, *cF96*; Hf<sub>0.71</sub>Os<sub>0.29</sub> (*ζ* phase) and Hf<sub>0.77</sub>Os<sub>0.23</sub> (*θ* phase), the last two of unknown structure. The determination of the structure of the *θ* phase has been included in this paper because of its evident relationship to the Sc<sub>57</sub>Rh<sub>13</sub> structure type.

**Experimental.** Annealing temperatures, refined cell parameters and conditions of their determination, of all phases discussed below, are listed in Table I while Table 2 should be consulted for information about data collection and structure refinement.\*

#### (a) Ordered Sc<sub>57</sub>Rh<sub>13</sub> and isotypic compounds

A sample of composition Sc<sub>57</sub>Rh<sub>13</sub> was prepared from sublimed Sc (99.95%) and Rh powder (99.9%) in an arc furnace under Ar atmosphere, and then wrapped

\* Lists of structure factors arranged in a standard crystallographic data file (Brown, 1983) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39892 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in a Ta foil and annealed for 8 d at 1023 K in a sealed quartz tube under 150 mm Ar. The stoichiometry of the ordered compound was deduced from our preliminary studies of the disordered variant of Sc<sub>57</sub>Rh<sub>13</sub>, observed in a non-annealed sample prepared at the composition Sc<sub>4</sub>Rh [see under (b)]. The structural analysis of this disordered phase, with space group *Im* $\bar{3}$ , led us to suspect the existence of an ordered phase which should have space group *Pm* $\bar{3}$ , same unit-cell volume and composition 57:13. The powder film made with a Guinier camera using graphite-monochromated Cu *Kα* radiation did indeed show additional weak diffraction lines with  $h+k+l = 2n+1$  at the *d* values calculated by the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). In order to obtain larger single crystals the sample was heated near the melting point and then allowed to cool slowly (see Table 1). The essential structural features of Sc<sub>57</sub>Rh<sub>13</sub> were found from the resolution of the disordered variant and the atomic and thermal parameters listed in Table 3 for ordered Sc<sub>57</sub>Rh<sub>13</sub> were refined from single-crystal data to a final *R* = 0.053.

Samples of Sc<sub>57</sub>Ru<sub>13</sub>, Sc<sub>57</sub>Ir<sub>13</sub> and Sc<sub>57</sub>Pt<sub>13</sub> were prepared in the arc furnace using previously melted Ru and Os powder (99.9%) and Pt wire (99.99%). The isotypy to the Sc<sub>57</sub>Rh<sub>13</sub> structure type was recognized from Guinier photographs.

#### (b) Disordered Sc<sub>57</sub>Rh<sub>13</sub> (Sc<sub>56.8</sub>Rh<sub>13.6</sub>)

A sample of nominal composition Sc<sub>4</sub>Rh was prepared in the arc furnace and a single crystal was isolated directly from the crushed melt and mounted on the automatic diffractometer. The Laue group was found to be *m* $\bar{3}$  and the systematic absences indicated a body-centred cell. The structure was solved by direct methods in space group *Im* $\bar{3}$ . The final composition from X-ray data was found to be Sc<sub>56.8</sub>Rh<sub>13.6</sub>; the structure contains some very close sites with fractional populations. The positional and thermal parameters of the nine sites listed in Table 3 [except for the temperature factor of Rh(2) which had to be held constant], together with the population parameters of four of them, were refined to a final *wR* = 0.025. The powder film of this unannealed sample of composition Sc<sub>4</sub>Rh does not contain any of the weak lines at  $h+k+l = 2n+1$  observed for the annealed sample prepared at the composition Sc<sub>57</sub>Rh<sub>13</sub> [see under (a)].

#### (c) Hf<sub>54</sub>Os<sub>17</sub>

An approximately single-phased sample of composition 77±1% Hf and 23±1% Os was kindly provided for us by Dr R. Waterstrat. It had been prepared from special Zr-free Hf and Os powder 99.9% (for chemical analysis of impurities see Waterstrat, 1983) in an arc furnace under a 50% Ar/50% He atmosphere, and annealed at 1823 K for 1½ h. Only a small crystal could be isolated and was measured on the

automatic diffractometer. Preliminary investigations indicated a body-centred orthorhombic cell with no other systematic absences than  $h+k+l = 2n+1$ . Since the Wilson test indicated a centric distribution of intensities space group  $Immm$  was chosen for the solution of the structure by direct methods. As it was not possible to distinguish between Hf and Os atoms on a difference electron density map the site occupation was determined from the examination of the interatomic

distances assuming that the shortest distances ( $d < 2.79 \text{ \AA}$ ) are between Hf and Os atoms. The resulting composition  $\text{Hf}_{0.761}\text{Os}_{0.239}$  is in good agreement with the electron microprobe analysis (Waterstrat, 1983). The positional and thermal parameters listed in Table 3 were refined to a final  $R = 0.084$ . Because of the small size of the crystal and the high absorption coefficients of Hf and Os only 21% of the 2300 collected unique reflections could be considered as observed.

Table 1. *Annealing conditions, unit-cell parameters and experimental conditions of their determination for  $\text{Sc}_{57}\text{Rh}_{13}$  and isotypic phases, disordered  $\text{Sc}_{57}\text{Rh}_{13}$  and  $\text{Hf}_{54}\text{Os}_{17}$*

Compound	Space group	Annealing conditions	Cell parameters* (e.s.d. in parentheses)	Radiation	Number of reflections	Limits on $2\theta$
$\text{Sc}_{57}\text{Ru}_{13}$	$Pm\bar{3}$	1023 K/11 d	$a = 14.394 (1) \text{ \AA}$	Cu $K\alpha\ddagger$	22	$33^\circ < 2\theta < 65^\circ$
$\text{Sc}_{57}\text{Rh}_{13}$	$Pm\bar{3}$	1213–1163 K†	$a = 14.4051 (7)$	Mo $K\alpha_1\ddagger$	18	$40^\circ < 2\theta < 58^\circ$
$\text{Sc}_{57}\text{Ir}_{13}$	$Pm\bar{3}$	1023 K/8 d	$a = 14.364 (1)$	Cu $K\alpha\ddagger$	28	$27^\circ < 2\theta < 67^\circ$
$\text{Sc}_{57}\text{Pt}_{13}$	$Pm\bar{3}$	923 K/8 d	$a = 14.415 (1)$	Cu $K\alpha\ddagger$	30	$27^\circ < 2\theta < 69^\circ$
$\text{Sc}_{57}\text{Rh}_{13}$ disordered	$Im\bar{3}$	as cast	$a = 14.414 (1)$	Mo $K\alpha_1\ddagger$	17	$31^\circ < 2\theta < 49^\circ$
$\text{Hf}_{54}\text{Os}_{17}$	$Immm$	1823 K/1½ h	$a = 13.856 (2)$ $b = 14.104 (2)$ $c = 14.570 (2)$	Mo $K\alpha_1\ddagger$	13	$41^\circ < 2\theta < 58^\circ$

\* The program *FINAX* (Hovestreydt, 1983) has been used for all refinements except for disordered  $\text{Sc}_{57}\text{Rh}_{13}$  where *PARAM* belonging to the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) has been used.

† The sample was first annealed at 1023 K/8 d and later heated to 1213 K for 1 h and allowed to cool slowly ( $10 \text{ K h}^{-1}$ ) to 1163 K.

‡ Automatic single-crystal X-ray diffractometer;  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ ,  $\lambda(\text{Cu } K\alpha_1) = 0.7093 \text{ \AA}$ .

§ Guinier–Nonius powder X-ray diffraction;  $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ , internal Si standard ( $a = 5.4307 \text{ \AA}$ ).

Table 2. *Experimental conditions for data collection and structure refinement for ordered  $\text{Sc}_{57}\text{Rh}_{13}$ , disordered  $\text{Sc}_{57}\text{Rh}_{13}$  ( $\text{Sc}_{56.8}\text{Rh}_{13.6}$ ) and  $\text{Hf}_{54}\text{Os}_{17}$*

	Ordered $\text{Sc}_{57}\text{Rh}_{13}$	Disordered $\text{Sc}_{57}\text{Rh}_{13}$	$\text{Hf}_{54}\text{Os}_{17}$
Shape of single crystal	Irregular	Irregular	Tabular ( $25 \times 25 \times 15 \text{ \mu m}$ )
Mean radius ( $\mu\text{m}$ )	25	27.5	11
Diffractometer		Automatic four-circle Philips PW 1100	
Radiation		Graphite-monochromated Mo $K\alpha$ ( $\lambda = 0.7107 \text{ \AA}$ )	
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Max. value $\sin\theta/\lambda$ ( $\text{\AA}^{-1}$ )	0.7028	0.7024	0.7029
$h, k, l$ ( $l \geq 0$ )	$h, k, l \leq 20$	$h, k, l \leq 20$	$h, k \leq 19; l < 20$
Antireflections	Yes	No	Yes
Standard reflections	583, 583	060, 060, 600	235, 235
Max. intensity variation	$\pm 2.7\%$	$\pm 1.6\%$	$\pm 5.2\%$
$\mu R$	0.233	0.260	1.615
Absorption correction (spherical)	$1.406 \leq A^* \leq 1.412$	$1.461 \leq A^* \leq 1.469$	$7.194 \leq A^* \leq 8.933$
Total number of reflections	3432	1595	4598
Unique reflections	1625	810	2299
$R_{\text{int}}$	0.029	0.027	0.046
Observed reflections	594	655	485
Criterion for recognizing 'less-thans'	$I \leq 3\sigma(I)$	$F \leq 3\sigma(F)$	$I \leq 3\sigma(I)$
Contributing reflections†	1013	735	1057
Ignored reflections	—	—	6, 1, 15, 2, 13, 9!
Refinement on	$ F $	$ F $	$ F $
Refined parameters	35	27	51
$R$	0.053	0.068	0.084
$wR$	0.051	0.025	—
$w$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	—
$S$	1.479	1.986	4.041
$\Delta/\sigma_{\text{max}}$ in final cycle	0.0010	0.0008	0.0004
Residual electron density ( $\text{e \AA}^{-3}$ )	$-5.27 \leq \text{r.e.d.} \leq 4.78$	$-3.74 \leq \text{r.e.d.} \leq 3.75$	$-38.8 \leq \text{r.e.d.} \leq 68.8\ddagger$
Programs used for structure solution	—	<i>MULTAN</i>	<i>SINGEN</i> , <i>TANGEN</i> ‡
All other programs used	<i>XRAY76</i> ‡	<i>XRAY76</i> ‡	<i>XRAY76</i> ‡
Atomic scattering factors	$c$	$c$	$c$

† Observed and 'less-thans' calculated greater than observed.

‡  $F(hkl) >> F(\bar{h}\bar{k}\bar{l})$ .

§  $68.8 \text{ e \AA}^{-3}$  at Os( $1A$ ), elsewhere  $39.1 \text{ e \AA}^{-3}$ .

|| Main *et al.* (1980).

‡ Stewart, Machin, Dickinson, Ammon, Heck & Flack (1976).

¶ Scattering factors for neutral atoms,  $f'$  and  $f''$  from *International Tables for X-ray Crystallography* (1974).

Table 3. Atomic coordinates and isotropic thermal parameters for ordered Sc<sub>57</sub>Rh<sub>13</sub>, disordered Sc<sub>57</sub>Rh<sub>13</sub> (Sc<sub>36</sub>Rh<sub>13,6</sub>) and Hf<sub>54</sub>Os<sub>17</sub>

E.s.d.'s are given in parentheses. The temperature factor is expressed as  $T = \exp[-2\pi^2 U(\sin^2\theta/\lambda^2)]$ . The sites are ordered and labelled in such a way as to facilitate the recognition of related sites in the three structures.

Ordered Sc <sub>57</sub> Rh <sub>13</sub> <i>Pm</i> $\bar{3}$				Disordered Sc <sub>57</sub> Rh <sub>13</sub> (Sc <sub>36</sub> Rh <sub>13,6</sub> ) <i>Im</i> $\bar{3}$				Hf <sub>54</sub> Os <sub>17</sub> <i>Immm</i>			
	x	y	z	x	y	z	U $\times 100$ (Å <sup>2</sup> )	x	y	z	U $\times 100$ (Å <sup>2</sup> )
Sc(1A)	24(0)	0-1122(2)	0-2978(2)	0-1135(1)	0-1844(1)	0-2952(1)	1-42(3)	16(0)	0-1170(4)	0-1806(4)	0-2861(4)
Sc(1B)	24(0)	0-6145(2)	0-7920(2)	0-1135(1)	0-1844(1)	0-2952(1)	1-42(3)	16(0)	0-1898(4)	0-3120(4)	0-1081(3)
Sc(2A)	12(0)	0	0-6758(4)	0	0-1770(2)	0-1084(1)	1-31(4)	16(0)	0-3086(4)	0-1132(3)	0-1787(3)
Sc(2B)	12(4)	†	0-6097(4)	0	0-1770(2)	0-1084(1)	1-31(4)	8(0)	0-1789(6)	0-1076(5)	0
Rh(1A)	12(0)	0	0-3337(2)	0	0-3339(1)	0-2028(1)	1-24(2)	8(0)	0-1094(6)	0-1848(6)	0-1693(6)
Rh(1B)	12(4)	†	0-8338(2)	0	0-3339(1)	0-2028(1)	1-24(2)	8(0)	0-3287(5)	0-2121(5)	0
Sc(3A)	12(0)	0	0-3915(3)	0	0-3921(3)	0-3711(3)	1-10(14)	8(0)	0-2001(5)	0-3320(5)	0-6(1)
Sc(4B)	12(4)	†	0-8257(3)	0	0-3921(3)	0-3711(3)	1-10(14)	8(0)	0-3760(6)	0-3906(6)	0-1-0(2)
Sc(5A)	6(c)	0-2271(5)	0	0-2255(5)	†	0	2-04(20)	8(0)	0-3993(5)	0	0-3345(5)
Sc(6A)	6(c)	0-3746(6)	0	0-1551(9)	†	0	1-00	4(0)	0-1889(10)	†	0-1631(8)
Sc(6B)	6(0)	0-8618(6)	†	0-1551(9)	†	0	1-33(7)	4(0)	0	0	0-3546(8)
Rh(3A)	1(0)	0	0	0-3687(2)	0	0	0-96(6)	4(c)	0-3908(9)	0	0-3(2)
Rh(3B)	1(0)	†	†	0	0	0	0-96(6)	2(0)	0	0	0-8(2)

\* The atom coordinates given do not correspond to the first entry for the Wyckoff point set but to a symmetry-equivalent position.

**Discussion.** Table 3 lists coordinates and isotropic thermal parameters.

#### Relationship between the Sc<sub>57</sub>Rh<sub>13</sub> and the Hf<sub>54</sub>Os<sub>17</sub> structures

The structural relationship between the cubic Sc<sub>57</sub>Rh<sub>13</sub>, *Pm* $\bar{3}$ , and the pseudo-cubic Hf<sub>54</sub>Os<sub>17</sub>, *Immm*, structures can be conveniently shown by comparing the positional parameters of these two structures with those of the disordered Sc<sub>57</sub>Rh<sub>13</sub> structure for which we found space group *Im* $\bar{3}$ . In Table 3 the atoms of the two ordered structures are labelled and their coordinates presented in such a way as to demonstrate their close geometrical relationship. It can be seen from this table that the Wyckoff positions of Sc(1), Sc(2), Sc(6) and Rh(1) in *Im* $\bar{3}$  have been split up in space groups *Pm* $\bar{3}$  and *Immm* in 2 and 3 positions respectively with only minor numerical changes in the atom coordinates ( $\frac{111}{222}$  should be added when comparing with the coordinates of the atoms in ordered Sc<sub>57</sub>Rh<sub>13</sub> whose labels contain B). Together with Rh(3), which also has its equivalent sites in the two ordered structures, these positions count for 110 atoms per unit cell which are common to the three structures. The main deviations from the cubic body-centred symmetry in the primitive orthorhombic structure occur at the sites derived from the atom sets which in disordered Sc<sub>57</sub>Rh<sub>13</sub> are only partially occupied. The different occupation of the sites related to the sites in the 12(e) position in *Im* $\bar{3}$  is also responsible for the difference in composition between the three structures. These two sites in disordered Sc<sub>57</sub>Rh<sub>13</sub>, one partially occupied by Sc [Sc(5)] and the other by Rh [Rh(2)], could theoretically have a total occupation of 12 atoms per unit cell together (not more because of the very small difference in the numerical values of the coordinates) but do in the real structure only count for an average of slightly less than seven atoms per unit cell. In ordered Sc<sub>57</sub>Rh<sub>13</sub>, on the other hand, one finds a Sc-occupied site of multiplicity 6 corresponding to the Sc(5) site whereas in Hf<sub>54</sub>Os<sub>17</sub> there are two fourfold sites [Os(2B) and Os(2C)] corresponding to the Rh(2) site.

Interatomic distances (*d*) up to 4 Å and their relative dilatation [ $\Delta = (d - \sum r) / \sum r$ ], using atomic radii for 12-coordinated atoms (Teatum, Gschneidner & Waber, 1960), have been calculated for the two ordered structures and the disordered structure variant. In neither of the two ordered structures is there any distance between minority atoms shorter than twice the atomic radii. In Sc<sub>57</sub>Rh<sub>13</sub> the shortest Sc-Sc distance is between atoms belonging to the Sc(4B) set,  $d = 2.964(7)$  Å ( $\Delta = -10\%$ ), while the shortest Sc-Rh distance can be found between Rh(1A) and one of its 11 closest neighbours  $\{d[\text{Sc}(3A)-\text{Rh}(1A)] = 2.541(5)$  Å,  $\Delta = -15\%$ . The same is true for Hf<sub>54</sub>Os<sub>17</sub>, considering the related sites Hf(4B) and Os(1A)  $\{d[\text{Hf}(4B)-\text{Hf}(4B)] = 2.791(10)$  Å,  $\Delta = -12\%$  and  $d[\text{Hf}(2A)-$

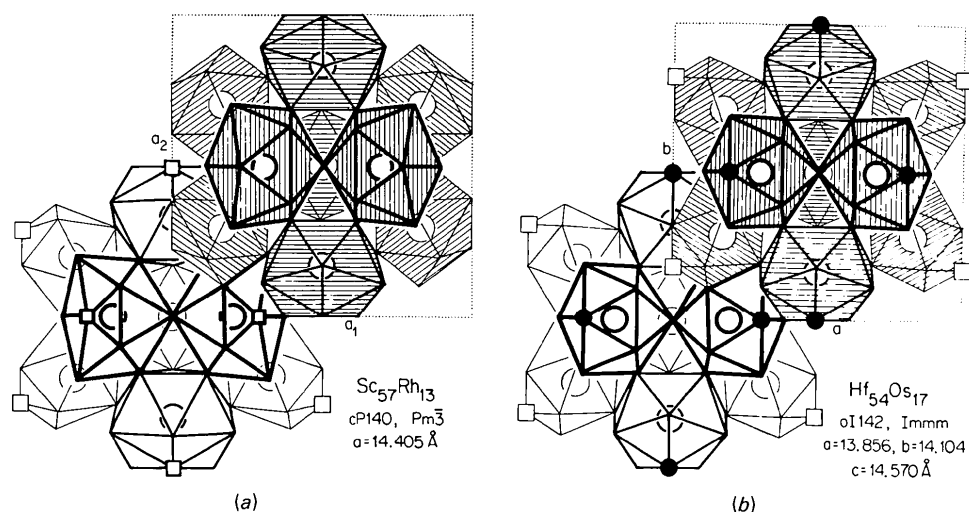


Fig. 1. 13-icosahedron units centred at  $000$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  in (a)  $\text{Sc}_{57}\text{Rh}_{13}$  and (b)  $\text{Hf}_{54}\text{Os}_{17}$ . The unit centred at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  in  $\text{Sc}_{57}\text{Rh}_{13}$  is a complete  $I_{114}C_{13}$  unit (see text) while all other units contain vacancies indicated by squares. The remaining icosahedron vertices are occupied by majority atoms except for those marked with a full circle in  $\text{Hf}_{54}\text{Os}_{17}$  which are occupied by Os atoms.

$\text{Os}(1A)| = 2.546(10) \text{ \AA}$ ,  $\Delta = -13\%$  respectively}. The coordination number of all of the smaller atoms is in both structures 12 [12 majority atoms for Rh(1B) and the sites related to Rh(3), 11 majority and 1 minority atoms for Os(1B) and Os(1C), 10 majority and 2 minority atoms for Os(2B) and Os(2C)], except for Rh(1A) and Os(1A) which have only 11, all majority, atoms at distances shorter than  $4 \text{ \AA}$ . The larger, Sc and Hf, atoms are coordinated by 12–15 atoms forming irregular, mixed polyhedra.

#### Description in terms of icosahedron units

One way of describing the two ordered structures consists in considering highly symmetrical structural units composed of 13 centred icosahedra where 12 outer icosahedra share vertices with a central one, the centres of the surrounding icosahedra being themselves icosahedrally arranged. Two kinds\* of such structural units, of compositions  $I_{114}C_{13}$  and  $I_{104}C_{13}$  respectively ( $I$  indicates the atoms forming the icosahedra and  $C$  the atoms centring these), will be discussed here. In the  $I_{114}C_{13}$  unit (shaded unit in Fig. 1a) the 12 outer icosahedra of the same unit are connected by their vertices while in the  $I_{104}C_{13}$  unit (Fig. 2) each outer icosahedron shares edges with 5 neighbouring outer icosahedra so that each of the atoms of these edges is in common to three outer icosahedra. By placing the centres of the 13-icosahedron units at the lattice points of a cubic body-centred Bravais lattice and by allowing

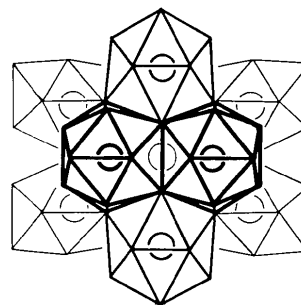


Fig. 2. 13-icosahedron unit of type  $I_{104}C_{13}$  as found around  $000$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  in  $\text{Mg}_{12}(\text{Al,Zn})_{49}$ : in the real structure several of the icosahedron vertices are occupied by C atoms.

the fusion either of triangular faces, edges or vertices with corresponding faces, edges or vertices of the neighbouring units [eight units displaced by  $\pm\frac{1}{2}$ ,  $\pm\frac{1}{2}$ ,  $\pm\frac{1}{2}$  and six displaced by  $\pm(100)Q$ ] hypothetical structures of composition  $I_{60}C_{13}$  and  $I_{68}C_{13}$  can be produced. The structures of  $\text{Sc}_{57}\text{Rh}_{13}$  and  $\text{Hf}_{54}\text{Os}_{17}$  are closely related to the former of these idealized structure models. It should be noted that the icosahedra in all the structures discussed here are slightly distorted in order to make these kinds of packing possible and that there also exist other icosahedrally coordinated sites in all of them.

*Hypothetical  $I_{60}C_{13}$  structure built up of  $I_{114}C_{13}$  units and derived structures.* The hypothetical structure of stoichiometry  $I_{60}C_{13}$ ,  $cI146$ , corresponds essentially to disordered  $\text{Sc}_{57}\text{Rh}_{13}$  but with atom sites Sc(3) and Rh(2) not existing and instead sites Sc(4) and Sc(5) fully occupied by  $I$  atoms. The composition  $I_{60}C_{13}$  can be obtained from the formula of one structural unit

\* Other kinds of units can be formed if the icosahedra have no common vertices. Such units (with uncentred icosahedra) are found in  $\beta$ -boron,  $hR324$ , (Hughes, Kennard, Sullenger, Weakliem, Sands & Hoard, 1963) and  $\text{YB}_{66}$ ,  $cF1608$ , (Richards & Kasper, 1969).

$I_{114}C_{13}$  by taking into account that some atoms are common to neighbouring structural units:

$$I_{60}C_{13} = I_{[114 - 6(2/2 + 4/3) - 8(6/2 + 6/3)]}C_{13}$$

In cubic primitive Sc<sub>57</sub>Rh<sub>13</sub> (Fig. 1a) there is a Sc<sub>14</sub>Rh<sub>13</sub> unit centred at  $\frac{111}{222}$  whereas the unit centred at 000 is incomplete. In this latter unit the 12 icosahedron vertices located the farthest from the unit centre and indicated by a square in Fig. 1(a) are not occupied [non-existence of an atom Sc(5B)]. In this way the central icosahedron at 000 is surrounded by 12 polyhedra with only 11 vertices and the resulting stoichiometry is 57:13 instead of 60:13.

In the orthorhombic body-centred Hf<sub>54</sub>Os<sub>17</sub> structure (Fig. 1b) the two structure units at 000 and  $\frac{111}{222}$  are identical but have lower point symmetry. The inner icosahedron here shares vertices with eight complete outer icosahedra where, however, the twelfth atom at the vertex situated the farthest from the unit centre is an Os instead of a Hf atom (indicated by full circles in Fig. 1b), and with four polyhedra having only 11 vertices as in the unit centred at 000 in Sc<sub>57</sub>Rh<sub>13</sub>.

*Hypothetical  $I_{68}C_{13}$  structure built up of  $I_{104}C_{13}$  units and derived structures.* The body-centred cubic structure built up from  $I_{104}C_{13}$  units (Fig. 2) contains 162 atoms per unit cell and has atom sites which correspond to those of the Mg<sub>32</sub>(Al,Zn)<sub>49</sub> structure (Bergman, Waugh & Pauling, 1957). As above, the stoichiometry can be calculated from the formula for one structural unit by considering that some atoms are common to neighbouring structural units:

$$I_{68}C_{13} = I_{[104 - 6(4/2) - 8(6/2)]}C_{13}$$

The compounds known to have the Mg<sub>32</sub>(Al,Zn)<sub>49</sub> structure type all have compositions different from  $I_{68}C_{13}$ ; however, in the case of Mg<sub>32</sub>(Al,Zn)<sub>49</sub> itself the sites corresponding to the centres of these icosahedra are richer in Al than all other sites having a mixed occupation of Al and Zn.

#### Structures containing similar polyhedron arrangements

The  $\beta$ -tungsten type of Cr<sub>3</sub>Si, *cP8*, is also characterized by an arrangement of icosahedra formed by the majority atoms and centred by the minority atoms. However, the linkage of these centred icosahedra is different from the structures discussed above. In the Cr<sub>3</sub>Si structure each centred icosahedron has 14 neighbouring icosahedra, sharing triangular faces with 8 of them and edges with 6 of them.

In YCd<sub>6</sub>, *cI168*, (Larson & Cromer, 1971)\* with a similar large body-centred cubic unit cell, the minority atoms are larger than the majority atoms and coordinated by 17 atoms (including the partially occupied

\* The structure was actually first solved for Ru<sub>3</sub>Be<sub>17</sub>, *cI160*, (Sands, Johnson, Krikorian & Kromholtz, 1962). In YCd<sub>6</sub> there is an extra site of multiplicity 24 which is only partially occupied and accounts for 8 extra atoms in the cell.

site near the origin). While a regular icosahedron is a pentagonal antiprism whose two pentagonal faces are capped by additional atoms, this 17-vertex polyhedron can be described in a similar way as being formed by two fused pentagonal antiprisms whose common pentagonal face is slightly larger and the two outer ones are capped by one atom each. In the YCd<sub>6</sub> structure the centres of these 17-vertex polyhedra are icosahedrally arranged in the same way as the centres of the outer icosahedra in the structural units discussed above. It can be seen from Fig. 3 that the outermost shell of the structural unit in YCd<sub>6</sub> is similar to that of the  $I_{114}C_{13}$  unit shown in Fig. 1(a).

#### Icosahedra in neighbouring phases in the phase diagrams

Alloys of early transition elements such as Sc, Ti, Zr or Hf with late transition elements of the Fe, Co or Ni groups often have structures with cubic unit cells, the number of atoms in the unit cell and the complexity of the structure increasing when moving towards the elementary constituents. For example in the particularly interesting system Sc–Ir all five binary phases known in the systems are cubic with 24 (MgCu<sub>2</sub> type), 2 (CsCl type), 120 (Sc<sub>11</sub>Ir<sub>4</sub> type), 140 (Sc<sub>57</sub>Rh<sub>13</sub> type) and 408 atoms (Mg<sub>44</sub>Rh<sub>7</sub> type) in the unit cell respectively. Icosahedra formed by the large Sc atoms and centred by the smaller Ir atoms are found in all types except for the CsCl type.

The Mg<sub>44</sub>Rh<sub>7</sub>, *cF408*, structure type was solved separately by Westin (1971) and Samson & Hansen (1972). The latter solved the structure on a phase in the Na–Ti system and used the approximate formula Na<sub>6</sub>Ti to denote it. The authors of both papers emphasize the fact that all minority atoms (Rh, Ti) are surrounded by icosahedra formed of majority atoms. Westin describes configurations formed by four to six icosahedra, while Samson & Hansen consider larger complexes where 14 icosahedra form six interpenetrating fivefold rings. Only 16 Mg (or Na) atoms of the 408 total atoms per unit cell do not participate in these complexes and form

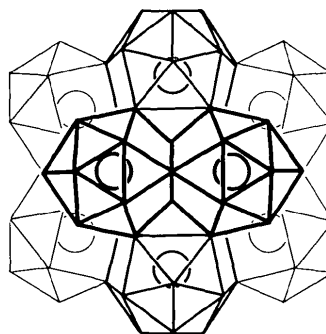


Fig. 3. Unit formed by twelve 17-atom polyhedra in YCd<sub>6</sub>. The Y atoms centring the polyhedra are icosahedrally arranged.

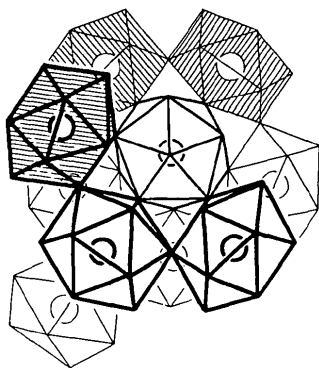


Fig. 4. 14-icosahedron unit in  $\text{Sc}_{44}\text{Os}_7$  and  $\text{Sc}_{44}\text{Ir}_7$  in a projection along  $[110]$ . The arrangement of the non-shaded icosahedra is similar to that found in the 13-icosahedron unit in  $\text{Sc}_5\text{Rh}_{13}$ .

isolated tetrahedra. It can be seen from Fig. 4, which shows the 14-icosahedra unit in isotypic  $\text{Sc}_{44}\text{Ir}_7$ , that 10 of the 14 icosahedra in the unit are arranged in a similar way to the 13-icosahedra complex shown in Fig. 1(a).

In the  $\text{Sc}_{11}\text{Ir}_4$  structure, *cF120*, (Chabot, Cenzual & Parthé, 1980a) there are three different sites occupied by Ir atoms: one is at the centre of a cube, the second at the centre of an octahedron and the third one is surrounded by 12 Sc atoms forming a polyhedron which can be considered as intermediate between a cuboctahedron and an icosahedron. These 12-vertex polyhedra share vertices and faces to form a three-dimensional net in which the interstices are occupied by the remaining Ir atoms.

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## Structure of Potassium [*meso*-2,3-Butanediaminetetraacetato(4–)]cobalt(III) 2.5 Hydrate, $\text{K}[\text{Co}(\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_8)] \cdot 2.5\text{H}_2\text{O}$

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**Abstract.**  $M_r = 459.3$ , orthorhombic, *Pbcn*,  $a = 29.361$  (22),  $b = 10.469$  (9),  $c = 11.535$  (8) Å,  $V = 3545$  (8) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.71$ ,  $D_x = 1.72$  Mg m<sup>-3</sup>,

$\text{Mo K}\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.98$  mm<sup>-1</sup>,  $F(000) = 1896$ , room temperature,  $R = 0.074$  for 1221 observed reflections [ $I \geq 1.96\sigma(I)$ ]. The structure consists of