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$Sc_{11}Ir_4$, $Sc_{11}Os_4$, $Sc_{11}Ru_4$ and $Zr_{11}Os_4$ with a New Cubic Structure Type Described by Means of a Cluster Concept

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Abstract

$Sc_{11}Ir_4$ and $Sc_{11}Os_4$ crystallize with a new cubic structure type in space group $Fm3m$ with $Z = 8$. $Sc_{11}Ir_4$: $a = 13{\cdot}350\ (4)$ Å, $D_x = 7{\cdot}05$ Mg m^{-3}, μ(Mo $K\alpha$) = 52·8 mm^{-1}, $F(000) = 4312$. $Sc_{11}Os_4$: $a = 13{\cdot}344\ (3)$ Å, $D_x = 7{\cdot}02$ Mg m^{-3}, μ(Ag $K\alpha$) = 27·3 mm^{-1}, $F(000) = 4280$. The final $R = 0{\cdot}055$ for $Sc_{11}Ir_4$ and 0·078 for $Sc_{11}Os_4$. $Sc_{11}Ru_4$ and $Zr_{11}Os_4$ have the same structure type. This new crystal structure is related to that of Th_6Mn_{23} or $Mg_6Cu_{16}Si_7$, but $Sc_{11}Ir_4$ has extra atoms located in the four octahedral voids. The structural relationship is shown by writing the chemical formulae in the following way: $Sc_6Sc_{16}Ir_8$, $Th_6Mn_{16}Mn_7\square$, $Mg_6Cu_{16}Si_7\square$. All these crystal structures can be described geometrically by means of clusters similar to those found in γ-brass or $Li_{22}Si_5$. Clusters here, however, are not isolated.

Introduction

Information on the Sc-rich parts of the phase diagrams containing Sc and transition elements of the Fe and Co group is scarce. Phase-diagram studies have been reported for Sc–Fe (Savitsky, Terekhova, Torchinova, Mavkova, Naumkin, Kolesnichenko & Stroganova, 1970) and Sc–Ru (Savitsky & Polyakova, 1975) which suggest that phases Sc_3Fe and Sc_3Ru should exist, but no structures have been given. Geballe, Matthias, Compton, Corenzwit, Hull & Longinotti (1965) made preliminary studies of the phases in the systems Sc–Rh and Sc–Ir and reported the phases Sc_3Rh and Sc_3Ir, but no attempt was made to solve their crystal structures. The only Sc_3T (T = transition element) structure known is Sc_3Co which may be described as a stacking variation of the Fe_3C and Re_3B structure types (Chabot & Parthé, 1978). It was of interest to find out whether the Sc_3Co type or a related structure type is also formed with the other Sc_3T compounds.

Experimental

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

Single crystals were isolated from crushed melts with starting compositions equivalent to Sc_3Ir and $Sc_{11}Os_4$. The true composition of Sc_3Ir was revealed later to be $Sc_{11}Ir_4$. The crystal of $Sc_{11}Ir_4$ was in the form of a trigonal prism (base: 50 × 50 × 60 μm, height: 110 μm); that of $Sc_{11}Os_4$ was irregular, mean diameter 50

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μm. The structures are cubic with the lattice parameters given in Table 1. According to the Laue group (*m*3*m*) and the lack of systematic extinctions other than those due to the Bravais lattice type, the possible space groups are *F*432, *F*$\bar{4}$3*m* or *Fm*3*m*. Data collection for $Sc_{11}Ir_4$ ($Sc_{11}Os_4$) was carried out on a Philips PW 1100 automatic four-circle diffractometer in the θ–2θ mode with graphite-monochromated Mo $K\alpha$ (Ag $K\alpha$) radiation, up to $\sin\theta/\lambda = 0{\cdot}7$ Å^{-1} (0·89 Å^{-1}), yielding 216 (379) independent reflexions. The $Sc_{11}Ir_4$ structure was solved by direct methods. The phases of 117 reflexions with $|E| > 0{\cdot}3$ were determined with *SINGEN* and *TANGEN* (XRAY system, 1976). Positional and isotropic thermal parameters refined satisfactorily with the full-matrix least-squares program *CRYLSQ* of the XRAY system. Intensities collected for $Sc_{11}Ir_4$ were corrected for absorption with *CAMEL JOCKEY* (Flack, 1975, 1977) and structure factors were corrected for isotropic secondary extinction. For $Sc_{11}Os_4$ only a spherical absorption correction was applied. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). Structure refinements were obtained from 172 (211) reflexions with $|F| > 3\sigma_F$. $R = \sum|\Delta F|/\sum|F_o| = 0{\cdot}055$ for $Sc_{11}Ir_4$ and 0·078 for $Sc_{11}Os_4$.* The final positional and isotropic thermal parameters are listed in Table 2, interatomic distances in Table 3. The space group is *Fm*3*m*; space groups *F*$\bar{4}$3*m* and *F*23 (with consideration of anomalous dispersion) have also been tested, but do not give any significant change in the positional parameters.

Table 1. *Lattice constants* (Å) *of phases with the* $Sc_{11}Ir_4$ *structure type* (*e.s.d.'s in parentheses*)

$Sc_{11}Ru_4$	13·367 (1)
$Sc_{11}Os_4$	13·344 (3)
$Sc_{11}Ir_4$	13·350 (4)
$Zr_{11}Os_4$	13·414 (4)

Isotypic compounds

The same crystal structure was also found for $Sc_{11}Ru_4$ which corresponds to the Sc_3Ru reported by Savitsky & Polyakova (1975). McCarthy & Schmidt (1971) investigated a section of the system Zr–Os and reported a cubic phase with a = 13·428 Å of composition $Zr_{11}Os_4$ and unknown structure. The similarity of lattice constant and composition led us to reinvestigate this phase; we can corroborate its existence. A simulated powder pattern calculated with *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) indicates isotypy with $Sc_{11}Ir_4$.

Table 3. *Interatomic distances* (Å) *in* $Sc_{11}Ir_4$ *and* $Sc_{11}Os_4$ *up to* 4 Å

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

$Sc_{11}Ir_4$		$Sc_{11}Os_4$	
Sc(1)–Ir(1)	2·663 (10)	Sc(1)–Os(1)	2·703 (18)
4Sc(3)	3·013 (4)	4Sc(3)	3·022 (4)
4Sc(2)	3·297 (9)	4Sc(2)	3·265 (15)
4Ir(3)	3·405 (3)	4Os(3)	3·395 (3)
4Sc(1)	3·766 (10)	4Sc(1)	3·822 (18)
Ir(2)	4·011 (10)	Os(2)	3·969 (18)
Sc(2)–Ir(2)	2·698 (5)	Sc(2)–Os(2)	2·689 (4)
3Ir(3)	2·959 (5)	3Os(3)	2·961 (4)
3Sc(2)	3·116 (8)	3Sc(2)	3·106 (10)
3Sc(3)	3·118 (7)	3Sc(3)	3·121 (11)
3Sc(1)	3·297 (9)	3Sc(1)	3·265 (15)
Sc(3)–3Ir(3)	2·735 (5)	Sc(3)–3Os(3)	2·733 (4)
3Sc(1)	3·013 (4)	3Sc(1)	3·022 (7)
3Sc(2)	3·118 (7)	3Sc(2)	3·121 (11)
3Sc(3)	3·523 (5)	3Sc(3)	3·516 (1)
Ir(1)	3·623 (4)	Os(1)	3·625 (5)
Ir(1)–6Sc(1)*	2·663 (10)	Os(1)–6Sc(1)*	2·703 (18)
8Sc(3)	3·623 (8)	8Sc(3)	3·625 (5)
Ir(2)–8Sc(2)†	2·698 (5)	Os(2)–8Sc(2)†	2·689 (4)
6Sc(1)	4·011 (10)	6Sc(1)	3·969 (18)
Ir(3)–4Sc(3)‡	2·735 (5)	Os(3)–4Sc(3)‡	2·733 (7)
4Sc(2)‡	2·959 (5)	4Sc(2)‡	2·961 (4)
4Sc(1)‡	3·405 (3)	4Sc(1)‡	3·395 (3)

* Octahedron.
† Cube.
‡ Cubo-octahedron.

Table 2. *The point positions of* $Sc_{11}Ir_4$ *and* $Sc_{11}Os_4$ *compared with those of* Th_6Mn_{23} *and* $Mg_6Cu_{16}Si_7$ (*space group Fm*3*m*)

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

		$Sc_{11}Ir_4$			$Sc_{11}Os_4$			Th_6Mn_{23}		$Mg_6Cu_{16}Si_7$	
			x	U (Å^2)		x	U (Å^2)		x		x
4(*a*)	0,0,0	Ir(1)		0·9 (1)	Os(1)		1·0 (1)	–		–	
4(*b*)	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	Ir(2)		1·0 (1)	Os(2)		0·5 (1)	Mn		Si	
24(*d*)	$0,\frac{1}{4},\frac{1}{4}$	Ir(3)		0·9 (1)	Os(3)		1·0 (1)	Mn		Si	
24(*e*)	*x*,0,0	Sc(1)	0·1995 (8)	1·3 (2)	Sc(1)	0·2026 (14)	1·2 (2)	Th	0·203	Mg	0·182
32(*f*)	*x*,*x*,*x*	Sc(2)	0·3833 (4)	1·0 (1)	Sc(2)	0·3837 (5)	0·7 (2)	Mn	0·378	Cu	0·377
32(*f*)	*x*,*x*,*x*	Sc(3)	0·1567 (3)	0·9 (1)	Sc(3)	0·1569 (6)	1·1 (2)	Mn	0·178	Cu	0·168

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* Lists of structure factors for $Sc_{11}Ir_4$ and $Sc_{11}Os_4$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34774 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The lattice constants of all four isotypic phases are given in Table 1. Cell parameters were obtained by least squares from 2θ values with *PARAM* (XRAY system, 1976). 2θ values were measured on films with a Debye–Scherrer camera (diameter 114·6 mm) and Cu $K\alpha$ radiation. Only back reflexions showing $K\alpha_1$ and $K\alpha_2$ resolution were considered. Cell parameters for $Sc_{11}Ir_4$ and $Sc_{11}Os_4$ were checked from the least-squares refinement of 2θ values of 30 reflexions obtained with the lattice-parameters-determination program of the diffractometer. Examination of the lattice constants shows that the variation of the a values does not agree with the variation of the metallic radii of the elements. $Sc_{11}Ru_4$ and particularly $Zr_{11}Os_4$ have unit cells which are relatively too large compared to those of $Sc_{11}Os_4$ and $Sc_{11}Ir_4$. As we shall see later, this paradox might possibly be due to the presence of small amounts of oxygen in these structures.

The superconducting transition temperatures of all four compounds have been investigated by Dr M. Ishikawa, University of Geneva. If the Sc compounds are superconducting at all, their transition temperature is below 1 K. $Zr_{11}Os_4$ showed at 4 K the conduction anomaly already described by McCarthy & Schmidt (1971).

Similarity with Th_6Mn_{23} and $Mg_6Cu_{16}Si_7$ type

As can be seen in Table 2, the point positions of $Sc_{11}Ir_4$ are virtually identical to those given for the Th_6Mn_{23} type (Florio, Rundle & Snow, 1952) or its ternary version $Mg_6Cu_{16}Si_7$ (Bergman & Waugh, 1956) except that the 4(a) sites are now occupied. The ternary phase is called the G phase in the Western literature (Spiegel, Bardos & Beck, 1963) but the T phase elsewhere (Markiv & Storozhenko, 1973). The last-mentioned authors report T phases for $Sc_6Al_{16}Ir_7$ (a = 12·31 Å) and $Sc_6Ga_{16}Ir_7$ (a = 12·43 Å) among others, and corresponding alloys with Os and Ru.

Polyhedron and cluster description

For the discussion of the $Sc_{11}Ir_4$ ($Sc_{11}Os_4$) structure we will first describe the individual coordination polyhedra of the atoms and then present a description based on clusters.

The atomic coordination numbers were evaluated by the gap criterion for the distribution of distances (Bruzzone, Fornasini & Merlo, 1970; Brunner & Schwarzenbach, 1971). The distribution around one atom was obtained by plotting the number of surrounding atoms at a distance d against the ratio $d/\sum r$, where $\sum r$ is equal to the sum of the metallic radii of the central atom and each of its surrounding atoms (r_{Sc} = 1·62, r_{Ir} = 1·36 and r_{Os} = 1·35 Å). For the Ir (Os) atoms one finds well defined gaps between the first coordination shell and atoms further away. Atoms in the first coordination shell have $d/\sum r$ values between 0·9 and 1·14. From Table 3 one can see that Ir(1) is surrounded by an octahedron and Ir(2) by a cube of Sc atoms. Ir(3) has 12 Sc neighbours in the form of a distorted cubo-octahedron. Except for Sc(2), which is surrounded by 13 neighbours ($0{\cdot}9 \le d/\sum r \le 1{\cdot}0$), no gaps are found for the other Sc atoms and no simple coordination figures can be recognized. In fact, the traditional description of individual atom polyhedra seems only of limited use for such a structure because it does not permit the complete structure to be understood.

It was thought interesting to search for larger structural units, not necessarily centred on an atom, which might allow the description of the whole structure in a simple manner. Recently the usefulness of such an attempt was demonstrated with $Sm_{11}Cd_{45}$ where the 448 atoms in the unit cell could be grouped into two types of clusters, both centred, one with 27 and the other with 29 atoms, which permitted a simple description (Fornasini, Chabot & Parthé, 1978). It is also known that γ-brass structures can be described by clusters of 26 atoms which are not centred by an atom (Pearson, Brandon & Brizard, 1976; Westman, 1972).

We find that $Sc_{11}Ir_4$ can be described by clusters of 26 or 27 atoms similar to those found in the structures cited above. However, the clusters in $Sc_{11}Ir_4$ are no longer isolated. All these clusters have the external shape of a cubo-octahedron. In $Sc_{11}Ir_4$ the six square (or rectangular) faces of one cubo-octahedron are shared with six neighbouring cubo-octahedra. Thus a framework of fused cubo-octahedra is formed. In $Sc_{11}Ir_4$ one observes the further peculiarity that there are two interpenetrating frameworks of fused cubo-octahedra which allow the $Sc_{11}Ir_4$ structure to be described as a cluster arrangement in two different ways depending on which sites have been assumed to be cluster centres.

(a) *Description based on fused γ-brass-like clusters* (*with additional* Ir *atoms in the interstices between the clusters*) (*Fig.* 1)

The clusters are centred at $\pm(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ + [F] [equipoint 8(c)] and consist of 26 atoms. They can be described as being built up from different polyhedra starting with an innermost tetrahedron (IT) of Sc(3) atoms, this being surrounded by an outer tetrahedron (OT) of Sc(2) atoms. The IT and OT tetrahedra are nested in an octahedron (OH) of Ir(3) atoms and finally the whole is surrounded by a cubo-octahedron (CO) of 12 Sc(1) atoms with rectangular (instead of square) faces. The polyhedral construction of these clusters (including the rectangular shape of the cubo-octahedron faces) is identical to that found in γ-brass clusters. However, in

$Sc_{11}Ir_4$ the OH and CO atoms are shared with neighbouring clusters. Fig. 1 shows a schematic drawing of two of these fused clusters, one being the mirror image of the other. Additional Ir atoms are found in the octahedral interstices formed between the clusters. Ir(1) are located in the small octahedral holes at (000) + [*F*] [equipoint 4(*a*); open circle in Fig. 1] and Ir(2) in the large octahedral holes at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ + [*F*] [equipoint 4(*b*); filled circle in Fig. 1]. In fact, It(2) have, as closest neighbours, eight Sc(2) atoms from the outer tetrahedra (OT) of the eight surrounding clusters.

(*b*) *Description based on two kinds of fused 27-atom clusters (with interstices between the clusters unoccupied)* (*Fig.* 2)

This description differs from that given above by a shift of origin. The centres of the new clusters shown in Fig. 2 are the filled and open circles shown in Fig. 1 [equipoints 4(*b*) and 4(*a*) respectively]. The cluster around Ir(2) (filled circles in Figs. 1 and 2) is similar to the cluster found in $Li_{22}Si_5$ (Fornasini, Chabot & Parthé, 1978) and consists of an Ir(2) atom at its centre (CC), a cube of Sc(2) atoms [in $Li_{22}Si_5$ one also finds a cube which is formed from the inner (IT) and outer (OT) tetrahedra having the same size], and an octahedron (OH) of Sc(1) atoms, the whole being surrounded by a cubo-octahedron of Ir(3) atoms. In contrast to the $Li_{22}Si_5$ cluster, the octahedron in $Sc_{11}Ir_4$ is larger and extends out from the cubo-octahedral faces. In $Li_{22}Si_5$ the clusters are isolated while in a $Sc_{11}Ir_4$ cluster the six square faces of the cubo-octahedron and the six corners of the octahedron are shared with six neighbouring cubo-octahedra and their inscribed six octahedra respectively. All the six neighbouring clusters belong to the second kind of 27-atom clusters.

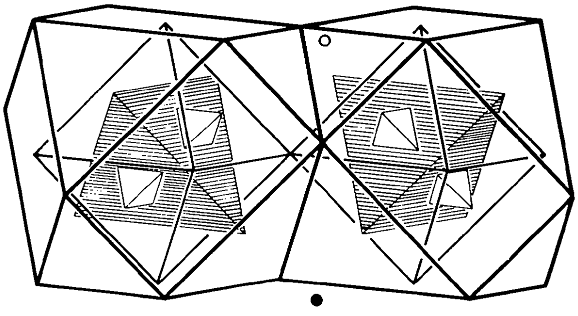

Fig. 1. The polyhedral construction of two fused 26-atom clusters in $Sc_{11}Ir_4$ centred at equipoint 8(*c*). The outermost cubo-octahedra (CO) are drawn with bold lines. Inscribed are octahedra (OH) with medium thin lines. Tetrahedra (IT and OT) are outlined with thin lines, the outer tetrahedra (OT) being shaded. Only two centres of the octahedral interstices between the clusters are indicated with circles (open circle: centre of a small octahedron; filled circle: centre of a large octahedron). All atoms are Sc atoms except those which are attached to the octahedra vertices and to the extra circles which are Ir atoms. In $Sc_6Al_{16}Ir_7$ with $Mg_6Cu_{16}Si_7$ structure type the filled circle and the octahedral vertices correspond to Ir atoms. Sc is located on the vertices of the cubo-octahedron, while the Al atoms are found on the vertices of the two tetrahedra. The open circle is unoccupied.

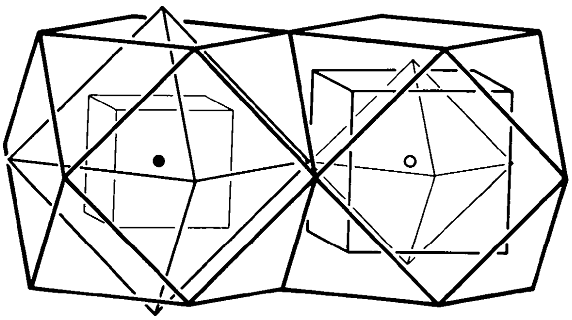

Fig. 2. The polyhedral construction of two fused 27-atom clusters in $Sc_{11}Ir_4$, centred at equipoints 4(*a*) and 4(*b*). The cluster similar to those found in $Li_{22}Si_5$ is shown on the left-hand side of the drawing. In the cluster on the right the sequence of the polyhedra is different; this sequence can be deduced from the different thicknesses of the corresponding lines. All atoms are Sc atoms except those found at cluster centres and cubo-octahedra vertices which are Ir atoms. In $Sc_6Al_{16}Ir_7$ the filled circle and the vertices of the cubo-octahedra correspond to the Ir sites, the vertices of the octahedron to the Sc sites and the vertices of the cube to the Al sites.

The clusters of the second kind are centred by Ir(1) atoms (open circles in Figs. 1 and 2). The polyhedron sequence is reversed here. The cluster centre (CC) is surrounded by a (smaller) octahedron of Sc(1) atoms, this being surrounded by a (larger) cube of Sc(3) atoms, all being surrounded by a cubo-octahedron (of the same size) of Ir(3) atoms. As above, the square faces of the cubo-octahedron and the corners of the octahedron are shared with neighbouring clusters which are now of the first kind.

The description of the $Sc_{11}Ir_4$ and Th_6Mn_{23} (or $Mg_6Cu_{16}Si_7$) structure types based on fused clusters is, of course, a purely geometrical approach in the understanding of the structure without consideration of the chemical bonding. Nevertheless, it is of interest to be able to describe a relatively complicated intermetallic phase structure as a simple packing of large polyhedral atom groupings.

On the presence of oxygen in the structure

Stabilization of the $Sc_{11}Ir_4$ structure type by oxygen cannot be completely excluded. Quantitative chemical analysis of the $Sc_{11}Ir_4$ melt, with an Exhalograph, showed that about four O atoms should be expected in one unit cell. However, no evidence of its existence in the structure could be found from electron density maps. Attempts to refine O atom population on different sites of the structure were made, but without success. We tested the improbable tetrahedral site centred at 8(c) and the pseudo octahedral site centred at 24(e) ($x \simeq 0{\cdot}35$) by least-squares refinement. Furthermore, the occupancy of each atomic site of the structure was independently tested, but in all cases this was found to be unity at the 2σ level. If the quantitative chemical analysis is correct, oxygen might possibly form small amounts of oxides in the melt in addition to the $Sc_{11}Ir_4$ phase. This hypothesis might be supported by the fact that X-ray powder patterns show weak reflexions which do not belong to the $Sc_{11}Ir_4$ phase (this point has been checked on a Gandolfi camera with the same single crystal as for the data collection) but unfortunately these additional lines could not be matched with any known phase containing these elements with or without oxygen.

In this context, it is of interest to note that in the system Zr–Os the $Zr_{11}Os_4$ phase competes with the phase having the Ti_2Ni structure type stabilized by N. A phase $Zr_4Os_2N_x$ (Ti_2Ni type with $a = 12{\cdot}37$ Å) has been reported by Holleck & Thümmler (1967).

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The Crystal Structure of $K_4(\beta_1\text{-}SiMoW_{11}O_{40}).9H_2O$

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Abstract

$K_4(\beta_1\text{-}SiMoW_{11}O_{40}).9H_2O$ is orthorhombic, space group *Pnma*, with $a = 20{\cdot}551$ (15), $b = 15{\cdot}535$ (12), $c = 12{\cdot}953$ (9) Å, $Z = 4$. The structure was determined from 2024 diffractometer intensities (Mo $K\alpha$ radiation) and refined to $R = 0{\cdot}052$. The structure is isomorphous with that of $K_4(\beta\text{-}SiW_{12}O_{40}).9H_2O$. The Mo atom is statistically distributed on three equivalent sites. Results are discussed with regard to both the α–β isomerism of the heteropolyanion and the geometrical isomerism in the β series.

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