

MgIr₃Si₇, a new magnesium iridium silicide with the ScRh₃Si₇ type structure**Peter Lorenz and Walter Jung***

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Correspondence e-mail:
walter.jung@uni-koeln.de**Key indicators**Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{Si}-\text{Si}) = 0.003$ Å
 R factor = 0.018
 wR factor = 0.044
Data-to-parameter ratio = 13.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, magnesium triiridium heptasilicide, was synthesized by reaction of the elemental components in a sealed tantalum container. It crystallizes in space group $R\bar{3}c$ and adopts the ScRh₃Si₇ structure type. Mg, Ir and one of the two crystallographically independent Si atoms are in special positions with site symmetries $\bar{3}$, 2 and 32, respectively. MgIr₃Si₇ shows metallic conductivity and remarkable chemical inertness.

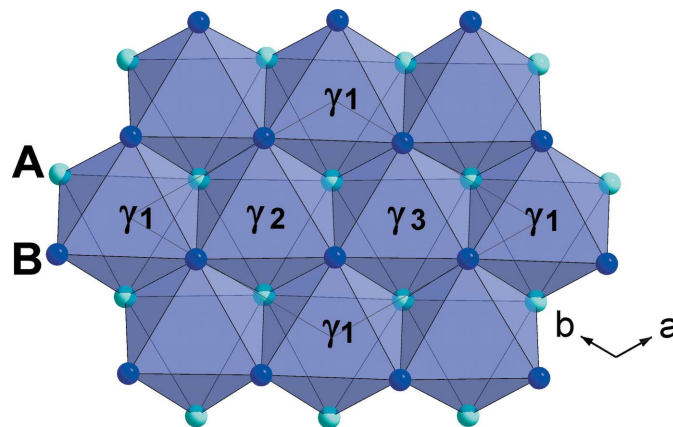
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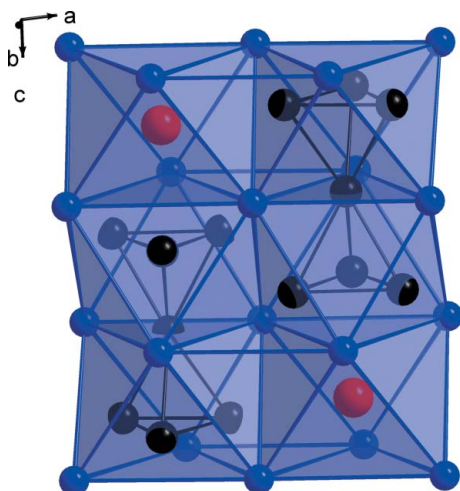
Comment

In the course of our studies of alkaline earth transition metal silicides, we were able to synthesize five ternary phases in the system Mg–Ir–Si: Mg₁₅Ir₅Si₂ (Lorenz *et al.*, 2002) and Mg₃Ir₃Si₈ (Jung, 2006) crystallize with their own structures, Mg₂IrSi (Schoolaert, 1995) is isotypic with Mg₂PtSi (Range *et al.*, 1990), and MgIrSi adopts the TiNiSi structure type (Shoemaker & Shoemaker, 1965). Here, we report on MgIr₃Si₇, which is isotypic with ScRh₃Si₇ and ScIr₃Si₇ (Chabot *et al.*, 1981).

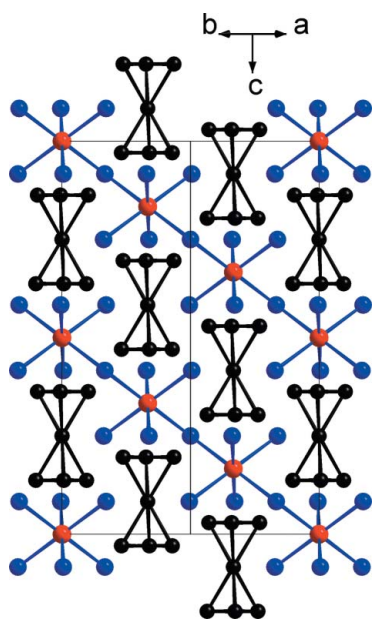
The ScRh₃Si₇ structure type has been described by Chabot *et al.* (1981). Following this description, the structure of the isotypic compound MgIr₃Si₇ may be interpreted on the basis of a hexagonal close-packed arrangement of the Ir atoms, with six layers per unit cell stacked along the c axis. However, the Ir–Ir distances, in the range 4.1248 (5)–4.4070 (6) Å, are far above the bonding distance. The Mg atoms occupy one third of the octahedral interstices in an ordered manner. Fig. 1 shows two layers of Ir atoms (A and B) forming a sheet of edge-connected octahedra. If the three possible positions for an octahedrally coordinated Mg atom in the ab plane are

**Figure 1**

The sheet of edge-connected octahedra formed by the stacking of two layers of Ir atoms A and B , in a projection along $[0001]$. The unit cell is outlined. Possible positions of the Mg atoms are denoted by $\gamma 1$, $\gamma 2$ and $\gamma 3$.


Figure 2

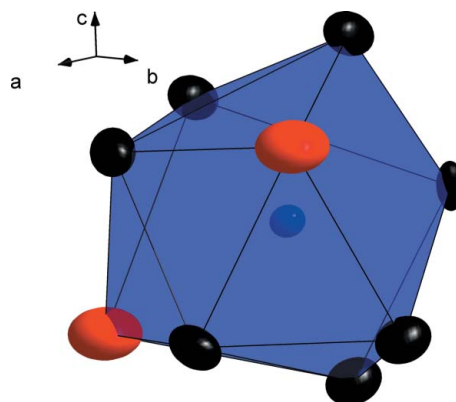
A section of the structure, showing the formation of Si_7 double tetrahedra by Si atoms centering one out of two triangular faces of every empty Ir octahedron. Mg atoms are red, Ir blue and Si black.


Figure 3

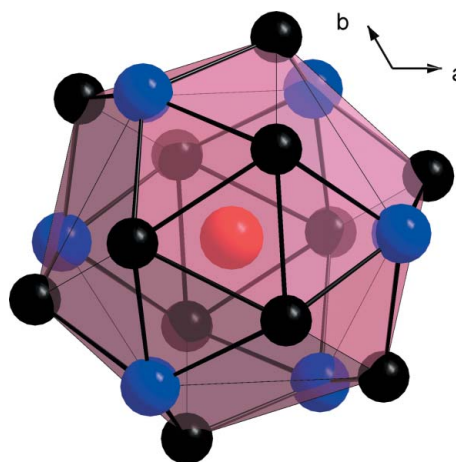
The arrangement of Si_7 double tetrahedra and MgIr_6 octahedra in a slab around the $(11\bar{2}0)$ plane. Colour code as in Fig. 2.

denoted by γ_1 , γ_2 and γ_3 , then the stacking sequence for Ir atoms (A , B) and Mg atoms (γ) can be expressed by $A\gamma_1B\gamma_2 A\gamma_3B\gamma_1 A\gamma_2B\gamma_3$.

As illustrated in Fig. 2, the Si atoms centre four of the eight triangular faces of every empty Ir_6 octahedron in such a way that Si_7 double tetrahedra are formed. Fig. 3 shows the arrangement of the MgIr_6 octahedra and the Si_7 double tetrahedra in a slab around the plane $(11\bar{2}0)$. The $\text{Si}\cdots\text{Si}$ distances in the double tetrahedra are 2.577 (3) ($\text{Si}1\cdots\text{Si}1^{\text{vi}}$) and 2.6980 (17) Å ($\text{Si}1\cdots\text{Si}2^{\text{vii}}$) (symmetry codes as in Table 1), much larger than the distance of 2.351 Å in elemental silicon (Toebbens *et al.*, 2001). Thus, only weak Si—Si bonding can be expected.


Figure 4

The environment of the Ir atoms, drawn with anisotropic displacement parameters at the 99% probability level. Colour code as in Fig. 2.


Figure 5

The environment of the Mg atoms. Colour code as in Fig. 2.

The shortest distances in the structure are those between the Si and Ir atoms. These are in the range 2.418 (2)–2.505 (2) Å and are thus close to the sum of the covalent radii, but considerably shorter than the sum of the metallic radii for coordination number (CN) 12 (2.438 and 2.730 Å, respectively; Pauling, 1973). Short distances between transition metals and Si atoms are frequently observed in binary and ternary silicides. In IrSi, for example, the Ir—Si distances range between 2.316 and 2.563 Å (Göransson *et al.*, 1995).

The environment of the Ir atoms, shown in Fig. 4, consists of seven Si and two Mg atoms and it is quite irregular. The $\text{Mg}\cdots\text{Ir}$ distance [3.040 (1) Å] and the $\text{Mg}\cdots\text{Si}$ distances [3.117 (2) and 3.144 (2) Å] are larger than the corresponding sums of the metallic radii for CN 12 (2.953 Å for Mg—Ir and 2.973 Å for Mg—Si; Pauling, 1973). This is possibly due to the large CN of 18 for the Mg atoms. The cage for the Mg atoms shown in Fig. 5 is formed by six Mg and 12 Si atoms.

Experimental

Single crystals of MgIr_3Si_7 were obtained from a mixture of the elemental components (Mg 99.8%, raspings prepared from a rod,

Ventron; Ir 99.9%, powder, Degussa; Si m4N, powder, Ventron) of composition MgIr_3Si_2 annealed at 1473 K for 3 d in a sealed tantalum tube under an argon atmosphere and cooled to room temperature at a rate of 5 K h^{-1} . For the synthesis of single phase MgIr_3Si_7 , a pre-alloy of composition Ir_3Si_7 was first prepared by arc melting under an argon atmosphere. The button obtained was crushed and powdered in a boron carbide mortar and mixed with the appropriate amount of magnesium raspings. The sample was annealed in a sealed tantalum tube under an argon atmosphere for 1 d and cooled to room temperature at a rate of 100 K h^{-1} . The product thus obtained was a grey sintered powder of remarkable chemical inertness. Even upon treatment with aqua regia, no attack was observed.

The temperature dependence of the resistivity of a sintered powder specimen was measured using a four-point DC device. The resistivity decreased nearly linearly from $4.3 \text{ m}\Omega \text{ cm}$ at 300 K to $3.2 \text{ m}\Omega \text{ cm}$ at 4.2 K. This is indicative of a poor metal.

Crystal data

MgIr_3Si_7	$D_x = 8.122 \text{ Mg m}^{-3}$
$M_r = 797.54$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}c$	$\mu = 62.33 \text{ mm}^{-1}$
$a = 7.5232 (8) \text{ \AA}$	$T = 294 (3) \text{ K}$
$c = 19.959 (3) \text{ \AA}$	Parallelepiped, black
$V = 978.3 (2) \text{ \AA}^3$	$0.06 \times 0.04 \times 0.03 \text{ mm}$
$Z = 6$	

Data collection

Stoe IPDS-I diffractometer	2857 measured reflections
ω scans	274 independent reflections
Absorption correction: numerical	241 reflections with $I > 2\sigma(I)$
[<i>X-RED</i> (Stoe & Cie, 2001), after optimizing the crystal shape using <i>X-SHAPE</i> (Stoe & Cie, 1999)]	$R_{\text{int}} = 0.048$
$T_{\text{min}} = 0.096$, $T_{\text{max}} = 0.306$	$\theta_{\text{max}} = 28.1^\circ$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$\Delta\rho_{\text{max}} = 1.28 \text{ e \AA}^{-3}$
$wR(F^2) = 0.044$	$\Delta\rho_{\text{min}} = -1.28 \text{ e \AA}^{-3}$
$S = 1.06$	Extinction correction: <i>SHELXL97</i>
274 reflections	(Sheldrick, 1997)
20 parameters	Extinction coefficient: $0.00157 (7)$
$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 9.1966P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected bond lengths (\AA).

Ir—Si1 ⁱ	2.4183 (18)	Mg—Si1 ^v	3.1168 (17)
Ir—Si2	2.4359 (4)	Mg—Si1 ^{vi}	3.1438 (18)
Ir—Si1 ⁱⁱ	2.4449 (17)	Si1—Si1 ^{vi}	2.577 (3)
Ir—Si1 ⁱⁱⁱ	2.5048 (17)	Si1—Si2 ^{vii}	2.6980 (17)
Ir—Mg ^{iv}	3.0398 (3)	Si2—Ir ^{viii}	2.4359 (4)

Symmetry codes: (i) $x - y + \frac{2}{3}, x - \frac{2}{3}, -z + \frac{1}{3}$; (ii) $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$; (iii) $-x + y + \frac{1}{3}, y - \frac{1}{3}, z + \frac{1}{6}$; (iv) $x + \frac{2}{3}, y + \frac{1}{3}, z + \frac{1}{3}$; (v) $-y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{1}{6}$; (vi) $-x + y, -x + 1, z$; (vii) $x + \frac{1}{3}, y + \frac{2}{3}, z - \frac{1}{3}$; (viii) $-x + y, -x, z$.

Lattice parameters were obtained from a Guinier pattern completely indexed on the basis of the single-crystal data [$\text{Cu } K\alpha_1$, $\lambda = 1.5406 \text{ \AA}$, Si as internal standard, least-squares refinement (Bach, 1978)]. The highest peak is located 1.27 \AA from Si1 and the deepest hole 0.76 \AA from Ir.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: Guinier film method (Bach, 1978); data reduction: *X-AREA* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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