The Crystal Structure of Ir_7Mg_{44}

LEIF WESTIN and LARS-ERIK EDSHAMMAR

*Institute of Inorganic and Physical Chemistry, University of Stockholm,
S-104 05 Stockholm 50, Sweden*

The most magnesium-rich compound in the iridium-magnesium
system, *viz.* Ir_7Mg_{44}, has been shown to be isomorphous with Rh_7Mg_{44}.
The structure is cubic with $a = 20.097$ Å and the space group is $F\bar{4}3m$.
The atomic parameters have been determined from Weissenberg
data. Interatomic distances and some special features of the structure
are discussed.

The iridium-magnesium system has been investigated by Ferro *et al.*[1] Phase
analyses by means of X-ray powder methods together with metallographic
and thermal studies showed that there are three intermetallic compounds in
the system, *viz.* $IrMg_3$, $IrMg_4$ and $IrMg_{\sim 6}$. The crystal structure was given
for $IrMg_3$ and was found to be of the Na_3As-type. No structural data were
given for $IrMg_4$, but $IrMg_{\sim 6}$ was found to be cubic with $a \approx 20$ Å.

The structural investigation described below shows that $IrMg_{\sim 6}$ is iso-
morphous to Rh_7Mg_{44}.[2,3]

EXPERIMENTAL

Samples of $IrMg_{6.3}$ were prepared from iridium powder and magnesium
filings (Johnson, Matthew & Co., 99.9 % pure). The components were mixed according
to the formula, and the mixtures were sealed in evacuated iron tubes. The iron tubes
were enclosed in silica tubes and were heated to 1100°C in a resistance furnace. The sam-
ples were kept at this temperature for one day and were then slowly cooled to 500°C
at a rate of two degrees per hour. The heat treatment was terminated by quenching
in water.

Powder photographs were obtained in a Guinier camera with $CuK\alpha_1$ radiation and
with KCl as an internal standard. The positions of the powder lines ($\sin^2 \theta_{obs}$) and the
observed intensities (I_{obs}) given in Table 1 were determined by the use of an automatic
film-scanner of Abrahamsson type [4] (a SAAB drum scanner [5] model 2 with a grid of
45 μm × 90 μm). A software system for the scanner connected to an IBM 1800 computer
has been developed at this institute [6] and modified for powder photographs of Guinier
type.[7]

The crystal used for the structure determination was a nearly rectangular parallel-
epiped with the edges approximately 0.02, 0.02, and 0.08 mm. Weissenberg photographs
were taken with rotation around an [110] axis using $CuK\alpha$ radiation. Five layer lines were
registered by the multiple-film technique and the intensities of 404 independent reflexions

Table 1. Guinier powder pattern of Ir_7Mg_{44} photographed with $CuK\alpha_1$ radiation. The intensities were recorded with an automatic film-scanner.

$\sum h^2$	$\sin^2 \theta_{obs} \times 10^5$	$\sin^2 \theta_{calc} \times 10^5$	I_{obs}	I_{calc} [a]
3	438	440	34	25
4	585	587	27	25
8	1 178	1 175	12	11
11	1 619	1 615	21	24
12	1 765	1 762	16	15
16	2 352	2 350	14	5
19	2 795	2 790	67	74
24	3 522	3 525	89	63
27	3 964	3 966	39	51
32	4 692	4 700	23	5
36	5 292	5 288	12	15
43	6 319	6 316	12	12
44	6 461	6 463	4	2
48	7 050	7 050	8	8
51	7 492	7 491	15	16
52	7 639	7 638	4	4
56	8 216	8 225	1	1
59	8 669	8 666	2	2
67	9 844	9 841	28	26
68	9 986	9 988	18	14
72	10 571	10 576	132	120
75	11 015	11 016	40	34
76	11 164	11 163	6	5
83	12 195	12 191	9	7
84	12 340	12 338	13	13
88	12 919	12 926	5	2
91	13 366	13 367	21	21
96	14 099	14 101	17	13
99	14 537	14 542	9	8
100	14 685	14 689	3	2
104	15 267	15 276	5	2
107	15 716	15 717	9	8
108	15 857	15 864	3	4
115	16 894	16 892	13	13
116	17 026	17 039	7	5
120	17 626	17 626	10	9
128	18 791	18 801	3	2
131	19 241	19 242	3	3
139	20 418	20 417	20	20
144	21 149	21 152	18	14
147	21 596	21 592	15	14
152	22 317	22 327	9	7
168	24 667	24 677	3	4
171	25 113	25 118	6	6
180	26 439	26 440	9	11
187	27 475	27 468	13	12
192	28 203	28 202	7	6
195	28 641	28 643	6	4
200	29 380	29 378	12	10
216	31 729	31 728	35	35
219	32 167	32 168	9	11
243	35 707	35 694	8	9
248	36 438	36 428	10	7
251	36 862	36 869	4	4
259	38 056	38 044	10	12

[a] The PLG (polarisation, Lorentz, and geometrical) factors are taken from the expression derived by Hägg and Regnström [8] for focusing powder cameras, modified to allow for monochromatic radiation.

Table 2. Computer programs used for the crystallographic calculations. All programs are written in FORTRAN IV.

Program name and function	Authors
LAZY. Calculation of $\sin^2\theta$- and d- values from the measured reflexion sites of a Guinier powder photograph after internal standard correction. IBM 360/75, IBM 1800.	A. G. Nord, Stockholm, Sweden.
PIRUM. Indexing of powder photographs and least squares refinement of unit cell parameters. IBM 1800.	P.-E. Werner, Stockholm, Sweden.
DATAP2. Lp- and absorption corrections. Preparative calculations for extinction correction according to Zachariasen's 1963-formula. IBM 360/75.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel. Modified by O. Olofsson and M. Elfström, Uppsala, Sweden. Inclusion of calculations for extinction correction by B. G. Brandt and S. Åsbrink, Stockholm, Sweden. Further modifications by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
LALS. Full matrix least squares refinement of positional and thermal parameters and of scale factors. IBM 360/75.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, Berkeley, USA, and by J.-O. Lundgren, R. Liminga and C.-I. Brandén, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg and by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations. IBM 360/75.	A. Zalkin, Berkeley, USA. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.

were estimated visually. Data were corrected for Lorentz, polarization and absorption effects ($\mu = 650$ cm^{-1}).

Computer programs, used for the crystallographic calculations, are listed in Table 2.

THE STRUCTURE OF Ir₇Mg₄₄

The powder photographs of IrMg$_{6.3}$ (*cf.* Table 1) showed the structure to be face-centered cubic. The cell constant refined by least-squares technique is $a = 20.097$ (1) Å.

A comparison between powder patterns and Weissenberg photographs obtained from IrMg$_{6.3}$ and Rh₇Mg₄₄ suggested that the two structures are isomorphous. The atomic parameters given for Rh₇Mg₄₄ were thus taken as a starting point for the refinement of the structure of the iridium compound. The refinement was performed by means of the least-squares technique. The final R-value was 0.091 with isotropic temperature factors and unit

Table 3. The final structure of Ir_7Mg_{44}. Space group $F\bar{4}3m$ (No. 216). Unit-cell content
8 Ir_7Mg_{44}.

Atom	Point positions	x	z	B (Å²)
Ir(1)	24 g	1/4	0.5867(1)	1.27(7)
Ir(2)	16 e	0.0839(2)		1.19(7)
Ir(3)	16 e	0.3482(1)		0.80(8)
Mg(1)	48 h	0.0517(9)	0.3385(12)	1.5(4)
Mg(2)	48 h	0.1067(8)	0.2147(12)	1.0(4)
Mg(3)	48 h	0.1928(8)	0.4799(12)	1.2(4)
Mg(4)	48 h	0.0985(9)	0.7194(12)	1.2(4)
Mg(5)	48 h	0.1561(8)	0.9797(10)	0.5(3)
Mg(6)	24 g	1/4	0.3561(14)	0.7(4)
Mg(7)	24 f	0	0.1814(18)	0.7(5)
Mg(8)	16 e	0.6973(10)		0.1(5)
Mg(9)	16 e	0.8338(10)		− 0.1(5)
Mg(10)	16 e	0.5623(12)		0.8(6)
Mg(11)	16 e	0.9482(14)		1.6(8)

weighting. The positional and the thermal parameters thus obtained are given in Table 3. The density calculated from the above given data is 3.95 g cm⁻³. The observed density calculated from the weight-difference of the alloy in chloroform and air is 3.93 (1) g cm⁻³.

DISCUSSION

The structure of Rh_7Mg_{44} [2,3] has recently been described as built up of a framework of magnesium icosahedra each of which encloses a rhodium atom. This framework comprises all the atoms of the structure except the Mg(10) atoms which form isolated Mg_4-tetrahedra. Studies by Samson and Hansen [9] have shown Na_6Tl to have the same type of structure. The present investigation has added Ir_7Mg_{44} as another member of this group of isomorphous phases.

A part of the Ir_7Mg_{44} structure is viewed along [001] in Fig. 1. Iridium atoms found between $z = 0.25$ and $z = 0.58$ are indicated by large numbered circles. The icosahedral shells around these iridium atoms are built up of magnesium atoms. Additional magnesium atoms, indicated by small circles, form tetrahedra around the positions $00\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the unit cell. The icosahedra surrounding iridium atoms at $z = 0.25$ and 0.41 form a complex of six icosahedra by sharing faces. One icosahedron around an iridium atom at $z = 0.16$ which belongs to this complex is concealed by the other atoms. Four icosahedra around $z = 0.42$ and $z = 0.58$ form a type of complex that is also found in the γ-brass type of structure.[10,11] Finally, icosahedra around $z = 0.35$ share corners with two additional icosahedra situated below the illustrated part of the structure. This arrangement of four icosahedra is also found in VAl_{10}.[12]

The structure of Ir_7Mh_{44} deviates very little from that of Rh_7Mg_{44}. Thus, the atomic coordinates of the Ir-phase deviate less than 0.003 from those of
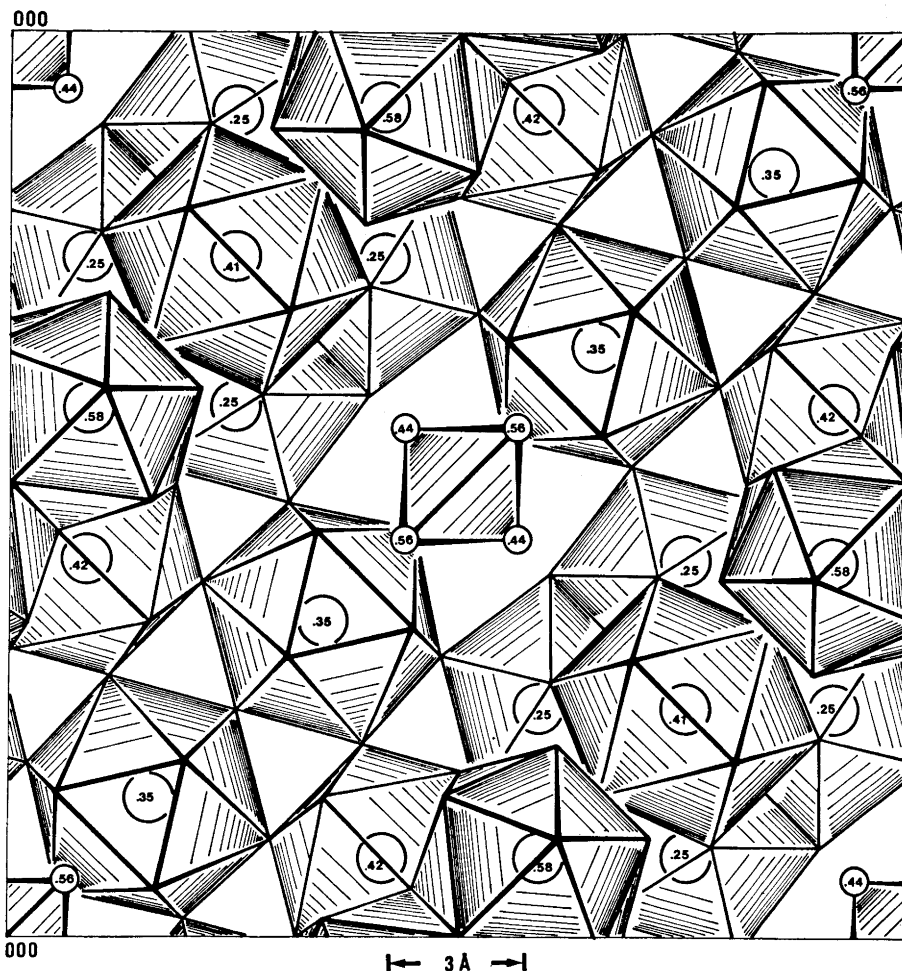
Fig. 1. Part of the Ir_7Mg_{44} structure seen along [001]. Iridium atoms are indicated by large circles. Small circles and corners of icosahedra are magnesium positions. The numbers indicate coordinates in the z direction.

the Rh-phase. The interatomic distances of Ir_7Mg_{44} are given in Table 4. The largest difference between corresponding distances in Ir_7Mg_{44} and Rh_7Mg_{44} is 0.11 Å (Mg(3) − Mg(3) and Mg(4) − Mg(4) contacts).

The atomic radius of iridium, found in the pure element, is about 0.01 Å larger than that of rhodium. In spite of this the cubic cell constant of Ir_7Mg_{44} is only 20.097 Å and thus 0.05 Å smaller than that of Rh_7Mg_{44} ($a = 20.148$ Å). Since the two structures are almost identical this difference may indicate that the structural details of these phases are influenced not only by atomic sizes but that the electronic structure may also affect the cell volume.

Table 4. Interatomic distances, coordination numbers and the type of the coordination polyhedra in Ir_7Mg_{44}.

Atom	No. of neighbours	Neighbour	Distance (Å)
Ir(1)	2	Mg(8)	2.68(1)[a]
	2	Mg(3)	2.69(2)
	2	Mg(9)	2.87(1)
	2	Mg(5)	2.99(2)
	4	Mg(4)	3.12(1)
	12, icosahedron		
Ir(2)	3	Mg(2)	2.71(2)
	3	Mg(11)	2.88(1)
	3	Mg(5)	2.93(2)
	3	Mg(7)	3.09(2)
	12, icosahedron		
Ir(3)	3	Mg(6)	2.80(1)
	3	Mg(1)	2.85(2)
	3	Mg(3)	2.89(2)
	3	Mg(2)	2.97(2)
	12, icosahedron		
Mg(1)	1	Ir(3)	2.85(2)
	1	Mg(2)	2.94(3)
	1	Mg(1)	2.94(5)
	2	Mg(3)	2.97(2)
	2	Mg(10)	3.05(2)
	2	Mg(1)	3.12(4)
	2	Mg(4)	3.37(3)
	1	Mg(7)	3.48(4)
	12, pentagonal prism + 2		
Mg(2)	1	Ir(2)	2.71(2)
	1	Mg(1)	2.94(3)
	1	Ir(3)	2.97(2)
	2	Mg(5)	2.98(2)
	2	Mg(6)	3.06(2)
	2	Mg(2)	3.07(3)
	2	Mg(3)	3.08(2)
	1	Mg(7)	3.11(2)
	12, pentagonal prism + 2		
Mg(3)	1	Ir(1)	2.69(2)
	1	Ir(3)	2.89(2)
	1	Mg(6)	2.97(3)
	2	Mg(1)	2.97(2)
	2	Mg(2)	3.08(2)
	2	Mg(4)	3.09(2)
	2	Mg(5)	3.23(2)
	1	Mg(3)	3.25(5)
	12, pentagonal prism + 2		

Table 4. Continued.

Mg(4)	1	Mg(8)	2.84(4)
	1	Mg(9)	3.00(3)
	2	Mg(3)	3.09(2)
	2	Ir(1)	3.12(2)
	2	Mg(5)	3.17(2)
	1	Mg(10)	3.32(4)
	2	Mg(1)	3.37(3)
	1	Mg(7)	3.44(3)
	2	Mg(4)	3.44(5)
	14, irregular polyhedron		
Mg(5)	1	Ir(2)	2.93(2)
	1	Mg(9)	2.95(3)
	2	Mg(2)	2.98(2)
	1	Ir(1)	2.99(2)
	1	Mg(11)	3.03(4)
	2	Mg(4)	3.17(2)
	2	Mg(7)	3.20(1)
	2	Mg(3)	3.23(2)
	12, pentagonal prism + 2		
Mg(6)	2	Ir(3)	2.80(1)
	2	Mg(3)	2.97(3)
	4	Mg(6)	3.02(3)
	4	Mg(2)	3.06(1)
	12, pentagonal prism + 2		
Mg(7)	2	Mg(11)	2.99(3)
	2	Ir(2)	3.09(2)
	2	Mg(2)	3.11(2)
	4	Mg(5)	3.20(1)
	2	Mg(4)	3.44(3)
	2	Mg(1)	3.48(4)
	14, irregular polyhedron		
Mg(8)	3	Ir(1)	2.68(1)
	3	Mg(4)	2.84(4)
	3	Mg(9)	2.88(3)
	3	Mg(8)	3.00(5)
	12, icosahedron		
Mg(9)	3	Ir(1)	2.87(1)
	3	Mg(8)	2.88(2)
	3	Mg(5)	2.95(3)
	3	Mg(4)	3.00(3)
	12, icosahedron		
Mg(10)	6	Mg(1)	3.05(2)
	3	Mg(4)	3.32(4)
	3	Mg(10)	3.54(4)
	12, twinned cubo-octahedron		
Mg(11)	3	Ir(2)	2.88(1)
	3	Mg(11)	2.94(5)
	3	Mg(7)	2.99(3)
	3	Mg(5)	3.03(4)
	12, icosahedron		

[a] The number given the corresponding Rh(1) in Rh₇Mg₄₄, *viz.* Rh(2), is a misprint.

The formulas Rh_7Mg_{44} and Ir_7Mg_{44} may be characterized as ideal ones corresponding to 100 % occupancy of the respective atomic sites of the structure. The ranges of homogeneity of these phases are not accurately known but are quite narrow. For some phases of the same or related structures regions of extended solid solubility have actually been found to exist. Thus, for a corresponding phase in the palladium – magnesium system Ferro [13] reported a range of homogeneity $PdMg_{5.6-6.8}$. The structure of this compound characterized by the formula $PdMg_6$ has been determined by Samson.[14] It is related to but clearly different from the Rh_7Mg_{44} type. On account of possibility of variable composition in the sodium-thallium compound and further isostructural compounds, which may exist, Samson prefers to describe the members of this family of structures as A_6B compounds. The ideal formula $A_{44}B_7$ corresponds to $A_{6.29}B$.

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