

Synthesis and Structure of RhMg₃ and Ir₃Mg₁₃

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Dedicated to Professor Evgen Ivanovich Gladyshevskii on the occasion of his 80th birthday

The binary transition metal magnesium compounds RhMg₃ and Ir₃Mg₁₃ have been synthesized from the elements in sealed niobium tubes and investigated on the basis of X-ray powder and single crystal data: Cu₃P type, $P6_3cm$, $a = 790.5(4)$, $c = 825.6(3)$ pm, $wR2 = 0.0244$, 344 F^2 values, 27 variable parameters for RhMg₃, and $R\bar{3}c$, $a = 1607.0(2)$, $c = 844.88(9)$ pm, $wR2 = 0.0535$, 656 F^2 values, 29 variable parameters for Ir₃Mg₁₃. The rhodium atoms in RhMg₃ have coordination number 11. These polyhedra show an AB AB stacking sequence like in the hexagonal close-packed structure. The crystal chemical relation of the Cu₃P type structure of RhMg₃ with the aristotype Na₃As (IrAl₃) is discussed on the basis of a group-subgroup scheme. Ir₃Mg₁₃ crystallizes with a new complex structure type with coordination numbers of 11, 14, 15, 14, and 12 for the Ir, Mg1, Mg2, Mg3, and Mg4 atoms, respectively.

Key words: Magnesium, Crystal Structure, Solid State Synthesis

Introduction

During our recent phase-analytical investigations of the magnesium-transition metal-indium systems [1–4], we obtained crystal chemical information on various binary transition metal-magnesium compounds. In the iridium based system the new equiatomic binary magnesium compound IrMg with a very complex crystal structure (Pearson code oC304) was discovered [5]. The ternary magnesium compounds Ir₃Mg_{13–x}In_x ($x = 2.37$ and 3.36) crystallize with a new rhombohedral structure type, space group $R\bar{3}c$. Our most recent investigations revealed, that this peculiar structure type also exists as a pure binary phase Ir₃Mg₁₃. In the binary Ir-Mg system, a compound of the approximate composition $\sim\text{IrMg}_4$ was already reported 40 years ago by Ferro *et al.* [6]. Most likely Ir₃Mg₁₃ corresponds to this phase. Attempts to synthesize an isotopic compound with rhodium resulted in a well crystallized sample of RhMg₃ with hexagonal Cu₃P type structure. The preparation and structure refinement of RhMg₃ and Ir₃Mg₁₃ are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of RhMg₃ and Ir₃Mg₁₃ were rhodium and iridium powder (Degussa-Hüls, 200 mesh, > 99.9%), and a magnesium rod (Johnson Matthey, \varnothing 16 mm, > 99.5%). Pieces of the magnesium rod (the surface of the rod was first cut on a turning lathe in order to remove surface impurities) and cold-pressed pellets of rhodium or iridium (\varnothing 6 mm) were weighed in the atomic ratios Rh:Mg and Ir:Mg = 3:13 and sealed in niobium ampoules under an argon pressure of about 800 mbar. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. Details about the arc-welding setup are given elsewhere [7]. The niobium tubes were placed in a water-cooled sample chamber [8] of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300). The mixtures of the elements were first heated under flowing argon up to ca. 1200 K. The reaction between the elements was visible through a slight heat flash. After the melting procedure the samples were cooled within one hour to ca. 700 K and finally quenched by switching off the furnace. The light gray samples could easily be separated from the niobium tubes. No reactions whatsoever of the samples with the crucible material could be detected. For the rhodium-based sample, a drop

Table 1. Crystal data and structure refinement for RhMg₃ and Ir₃Mg₁₃.

Empirical formula	RhMg ₃	Ir ₃ Mg ₁₃
Formula weight	175.84 g/mol	892.63 g/mol
Unit cell dimensions	$a = 790.5(4)$ pm $c = 825.6(3)$ pm $V = 0.4468$ nm ³	$a = 1607.0(2)$ pm $c = 844.88(9)$ pm $V = 1.8900$ nm ³
Pearson symbol	hP24	hR96
Structure type	Cu ₃ P	new
Space group	$P6_3cm$	$R\bar{3}c$
Formula units / cell	$Z = 6$	$Z = 6$
Calculated density	3.92 g/cm ³	4.71 g/cm ³
Crystal size	25 × 30 × 40 μm ³	30 × 40 × 65 μm ³
Transmission ratio (max/min)	1.41	1.94
Absorption coeff.	6.0 mm ⁻¹	32.2 mm ⁻¹
F(000)	486	2322
Detector distance	—	90 mm
Exposure time	—	12 min
ω Range; increment	—	0–180°, 1.0°
Integr. parameters A, B, EMS	—	13.0, 2.5, 0.01
θ Range for data collection	2° to 31°	2° to 31°
Range in hkl	$\pm 11, \pm 11, -11 \leq l \leq 3$	$\pm 23, \pm 23, \pm 12$
Total no. of reffs	3221	6547
Independent reffs	344 ($R_{\text{int}} = 0.0469$)	656 ($R_{\text{int}} = 0.0687$)
Reflections with $I > 2\sigma(I)$	308 ($R_{\text{sigma}} = 0.0165$)	611 ($R_{\text{sigma}} = 0.0259$)
Twin ratio; BASF parameter	0.47(10)	—
Data / parameters	344 / 27	656 / 29
GooF on F^2	1.178	1.067
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0122$ $wR2 = 0.0225$	$R1 = 0.0247$ $wR2 = 0.0524$
R Indices (all data)	$R1 = 0.0187$ $wR2 = 0.0244$	$R1 = 0.0283$ $wR2 = 0.0535$
Extinction coeff.	0.0054(2)	0.00022(3)
Largest diff. peak and hole	0.48 and -0.40 e/Å ³	2.82 and -1.47 e/Å ³

of magnesium had distilled to the colder, upper part of the tube, already indicating that a compound with a lower magnesium content had formed. Both samples are stable in moist air as compact pieces as well as fine-grained powders. Single crystals exhibit metallic luster. The polycrystalline samples are very brittle.

Scanning electron microscopy

Selected single crystals have been analyzed by EDX measurements using a LEICA 420 I scanning electron microscope with MgO, rhodium, and iridium as standards. No impurity elements were detected. The analyses revealed the compositions 25 ± 2 at.-% Rh : 75 ± 2 at.-% Mg and 19 ± 2 at.-% Ir : 81 ± 2 at.-% Mg, close to the ideal compositions 25 at.-% Rh : 75 at.-% Mg and 18.8 at.-% Ir : 81.2 at.-% Mg for RhMg₃ and Ir₃Mg₁₃, respectively.

Table 2. Atomic coordinates and isotropic displacement parameters (pm²) for RhMg₃ and Ir₃Mg₁₃. U_{eq} is defined as one third on the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff position	x	y	z	U_{eq}
RhMg₃ (space group $P6_3cm$)					
Rh	6c	0.32789(7)	x	0.2487(6)	90(1)
Mg1	2a	0	0	0.3119(6)	135(9)
Mg2	4b	1/3	2/3	0.2047(4)	199(10)
Mg3	6c	0.2865(3)	x	0.5764(2)	137(5)
Mg4	6c	0.6262(3)	x	0.4193(3)	162(5)
Ir₃Mg₁₃ (space group $R\bar{3}c$)					
Ir	18e	0.17340(2)	0	1/4	118(1)
Mg1	18e	0.6290(2)	0	1/4	165(5)
Mg2	6a	0	0	1/4	218(10)
Mg3	36f	0.4922(2)	0.1907(2)	0.9114(2)	223(4)
Mg4	18d	1/2	0	0	202(6)

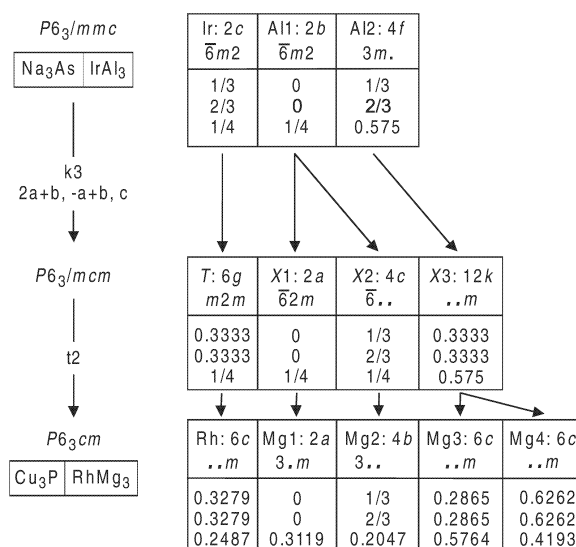


Fig. 1. Group-subgroup scheme in the Bärnighausen formalism [18, 19] for the structures of IrAl₃ (Na₃As type) and RhMg₃ (Cu₃P type). The indices of the *klassengleiche* (k) and *translationengleiche* (t) transitions, as well as the unit cell transformations are given.

X-ray film data and structure refinement

The samples were characterized through their Guinier powder patterns using Cu-K α_1 radiation and α -quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The Guinier camera was equipped with an imaging plate system (Fujifilm BAS-1800). The lattice parameters (Table 1) were obtained from least-squares fits of the Guinier data. To ensure correct indexing, the observed patterns were compared to calculated ones [9] using the atomic positions obtained from the structure refinements. The lattice parameters derived for the powders and the single crystals agreed well.

Table 3. Interatomic distances (pm) in the structures of RhMg₃ and Ir₃Mg₁₃ calculated with the lattice parameters obtained from the Guinier powder data.

RhMg ₃				Ir ₃ Mg ₁₃			
Rh:	1	Mg1	264.4(2)	Ir:	2	Mg3	270.6(2)
	2	Mg2	268.1(2)		2	Mg4	271.9(1)
	1	Mg3	272.6(6)		2	Mg1	272.0(1)
	1	Mg4	274.4(6)		1	Mg2	278.7(1)
	1	Mg4	274.7(4)		2	Mg3	281.7(2)
	2	Mg3	282.8(3)		2	Mg3	340.7(3)
Mg1:	2	Mg4	312.6(3)	Mg1:	2	Ir	272.0(1)
	1	Mg3	336.4(4)		2	Mg4	295.9(2)
	3	Rh	264.4(2)		2	Mg1	300.6(2)
	3	Mg3	298.5(4)		2	Mg3	301.3(2)
	3	Mg4	308.5(3)		2	Mg4	310.8(2)
	3	Mg3	314.6(4)		2	Mg3	369.6(4)
Mg2:	3	Rh	268.1(2)	Mg2:	2	Mg3	373.8(4)
	3	Mg3	303.0(3)		3	Ir	278.7(1)
	3	Mg4	305.6(3)		6	Mg3	296.6(2)
	3	Mg4	342.9(4)		6	Mg3	379.1(2)
Mg3:	1	Rh	272.6(6)	Mg3:	1	Ir	270.6(2)
	2	Rh	282.8(3)		1	Ir	281.7(2)
	1	Mg4	291.3(2)		2	Mg3	290.3(3)
	2	Mg4	297.5(2)		1	Mg2	296.6(2)
	1	Mg4	298.3(4)		1	Mg1	301.3(2)
	1	Mg1	298.5(4)		1	Mg3	303.8(4)
Mg4:	2	Mg2	303.0(3)	Mg4:	1	Mg4	315.5(3)
	1	Mg1	314.6(4)		1	Mg4	321.4(2)
	1	Rh	336.4(4)		1	Mg4	321.8(2)
	1	Rh	274.4(6)		1	Ir	340.6(3)
	1	Rh	274.7(4)		1	Mg1	369.6(4)
	1	Mg3	291.3(2)		1	Mg1	373.8(4)
	2	Mg3	297.5(2)		1	Mg2	379.1(2)
	1	Mg3	298.3(4)		2	Ir	271.9(1)
	2	Mg2	305.6(3)		2	Mg1	295.9(2)
	1	Mg1	308.5(3)		2	Mg1	310.8(2)
	2	Rh	312.6(3)		2	Mg3	315.5(2)
	2	Mg2	342.9(4)		2	Mg3	321.4(2)
					2	Mg3	321.8(2)

Irregularly shaped single crystals of RhMg₃ and Ir₃Mg₁₃ were isolated from the annealed samples by mechanical fragmentation and first examined by Laue photographs on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection. Intensity data of RhMg₃ were recorded at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized Mo-K α radiation ($\lambda = 71.073$ pm) and a scintillation counter with pulse-height discrimination. The scans were taken in the $\omega/2\theta$ mode and an empirical absorption correction was applied on the basis of psi-scan data. The data set for Ir₃Mg₁₃ was collected on a Stoe IPDS-II diffractometer with graphite monochromatized Mo-K α radiation. The absorption correction for this crystal was numerical. All relevant crystallographic data for the data collections and evaluations are listed in Table 1.

The isotypy of RhMg₃ with Cu₃P (space group $P6_3cm$) and of Ir₃Mg₁₃ (space group $R\bar{3}c$) with the ternary compounds Ir₃Mg_{13-x}In_x ($x = 2.37$ and 3.36) was already evident from the X-ray powder data. The atomic positions of IrMg_{2.03}In_{0.97} [2] and Ir₃Mg_{10.63}In_{2.37} [3] were taken as starting values and both structures were successfully refined using SHELXL-97 (full-matrix least-squares on F_o^2) [10] with anisotropic atomic displacement parameters for all sites. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. The occupancy parameters varied between 97(1)% for the Mg1 site of RhMg₃ and 102(2)% for the Mg1 and Mg2 sites of Ir₃Mg₁₃. Thus, all sites were fully occupied within three standard deviations. In the final cycles, the ideal occupancies were assumed again. The last cycles for RhMg₃ were calculated with the setting derived from the group-subgroup scheme (Fig. 1). A *translationengleiche* symmetry reduction (t2) suggested the possibility of twinning by inversion and actually was observed for the investigated single crystal. Final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Listings of the observed and calculated structure factors are available.*

Discussion

Binary RhMg₃ has so far only been reported in a theoretical study by Blyth *et al.* [11]. These authors studied co-sputtered films of binary transition metal (*T*)–magnesium alloys with photoemission with respect to the *d*-band occupancy of the transition metal.

The problem of all older reports on the TMg₃ ($T = \text{Pd, Pt, Ir, Au}$) [12–14] phases was the assignment of the correct structure type. In the older work, only the smaller Na₃As type subcell, space group $P6_3/mmc$, had been reported on the basis of X-ray powder data.

Indeed, the TMg₃ ($T = \text{Pd, Pt, Ir, Au}$) compounds crystallize with a superstructure of the Na₃As type. The cell enlargement was already observed by X-ray powder diffraction by Daams and van Vucht for AuMg₃ [15] and later by Range and coworkers by single crystal data for PtMg₃, IrMg₃, and AuMg₃ [16, 17].

In Fig. 1 we present the corresponding group-subgroup scheme [18, 19]. The Zintl phase Na₃As [20], space group $P6_3/mmc$, is the aristotype. IrAl₃ [21] adopts the same structure. The first step of the symmetry reduction is the *klassengleiche* transition of

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD 413720 (RhMg₃) and CSD 413721 (Ir₃Mg₁₃).

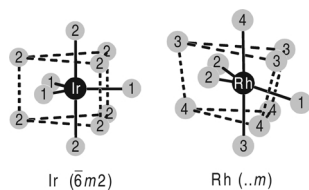


Fig. 2. The near-neighbor environment of iridium and rhodium in the structures of IrAl₃ and RhMg₃. Iridium (rhodium) and magnesium (aluminium) atoms are drawn as filled and gray circles, respectively. The shorter Ir–Al and Rh–Mg contacts are drawn with thick bonds. Atom designations and site symmetries are given.

index 3 (k3) to space group $P6_3/mcm$, followed by de-centering (t2) to $P6_3cm$ (structure type Cu₃P). These symmetry reductions lead to four crystallographically independent magnesium positions. The structural distortion of the TMg₃ compounds with respect to IrAl₃ is most likely due to the larger difference in size between Rh and Mg as compared to Ir and Al.

The structural distortions in the superstructure are quite pronounced. As already described for IrMg_{2.03}In_{0.97} [2], the rhodium and iridium atoms in IrAl₃ and RhMg₃ are hexagonally close packed. They have both eleven nearest aluminium, respectively magnesium neighbors in the form of pentacapped trigonal prisms (Fig. 2). Consequently both structures can be described by an AB AB stacking of these IrAl₁₁ and RhMg₁₁ polyhedra.

Ir₃Mg₁₃ (\equiv IrMg_{4.33}) crystallizes with a new structure type, Pearson symbol hR96. Most likely this phase corresponds to \sim IrMg₄, reported 40 years ago by Ferro *et al.* [6]. This Ir₃Mg₁₃ type has been observed first in the ternary system iridium-magnesium-indium for two crystals of the solid solution Ir₃Mg_{13–x}In_x with

$x = 2.37$ and 3.36 [3]. In our recent manuscript we have discussed the complicated structure in detail. Consequently we give only a brief description here. The lattice parameters and the cell volumes of binary Ir₃Mg₁₃ and the ternary compounds Ir₃Mg_{13–x}In_x with $x = 2.37$ and 3.36 are almost identical. The magnesium/indium mixing has only a minor influence on these parameters. Nevertheless, we observe small differences in the atomic positions. This shift in the atomic parameters from Ir₃Mg₁₃ via Ir₃Mg_{10.63}In_{2.37} to Ir₃Mg_{9.64}In_{3.36} nicely correlates with the indium content. The Ir, Mg1, Mg2, Mg3, and Mg4 atoms have coordination numbers 11, 14, 15, 14, and 12, respectively. These polyhedra show a complex intergrowth in the relatively large unit cell as presented in [3].

The shorter Rh–Mg and Ir–Mg distances range from 264 to 283 pm in RhMg₃, and from 271 to 282 pm in Ir₃Mg₁₃. They are only slightly larger than the sum of the covalent radii of 261 (Rh + Mg) and 262 pm (Ir + Mg) [22]. We can thus assume significant transition metal–magnesium bonding in these intermetallics. The Mg–Mg distances cover large ranges in RhMg₃ (291–343 pm) and Ir₃Mg₁₃ (290–379 pm). Most Mg–Mg distances are significantly shorter than in *hcp* magnesium (320 pm average Mg–Mg distance) [23]. Thus, strong Mg–Mg interactions dominate the chemical bonding in these magnesium rich intermetallics.

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