

# The magnesium-rich intermetallics $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$ and $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$

Viktor Hlukhyy, Rainer Pöttgen\*

*Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 36, D-48149 Münster, Germany*

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## Abstract

Phase analytical investigations in the system magnesium–iridium–indium revealed the magnesium-rich intermetallics  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$  and  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$ . The samples were prepared from the elements via induction melting in glassy carbon crucibles in a water-cooled sample chamber and subsequent annealing. Both intermetallics were investigated by X-ray powder and single-crystal diffraction:  $C2/c$ ,  $Z = 4$ ,  $a = 979.1(1)$ ,  $b = 2197.4(2)$ ,  $c = 848.2(1)$  pm,  $\beta = 105.79(1)^\circ$ ,  $wR_2 = 0.0434$ , 3076  $F^2$  values, 108 variables for  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$ , and  $a = 983.39(8)$ ,  $b = 2211.4(2)$ ,  $c = 849.55(7)$  pm,  $\beta = 105.757(6)^\circ$ ,  $wR_2 = 0.0487$ , 3893  $F^2$  values, and 115 variables for  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$ . Both compounds show solid solutions. In  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$ , the indium site shows an occupancy by 69.9(4)% In + 30.1(4)% Ir, and one magnesium site has a small mixed occupancy with indium, while nine atomic sites in  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$  show Mg/In mixing with indium occupancies between 1.2(3)% and 14.8(3)%. The relatively complex crystal structure is of a new type. It can be explained by a packing of coordination number 10 and 12 polyhedra around the iridium atoms. The crystal chemical peculiarities and chemical bonding in both intermetallics is briefly discussed.

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**Keywords:** Intermetallic compounds; Crystal structure; Indium

## 1. Introduction

Our recent phase analytical investigations in the ternary system magnesium–iridium–indium revealed extended solid solutions for several of the binary phases:  $\text{IrIn}_{2-x}\text{Mg}_x$  [1] and  $\text{IrIn}_{3-x}\text{Mg}_x$  [2] for the binary iridium–indium compounds and  $\text{IrMg}_{3-x}\text{In}_x$  [1] and  $\text{Ir}_3\text{Mg}_{13-x}\text{In}_x$  [3] for the magnesium-rich iridium compounds. So far, our attempts to prepare ternary compounds which do not derive from the binaries via a simple solid solution failed. Also the phases  $\text{Ir}_3\text{Mg}_{13-x}\text{In}_x$  ( $x = 2.37$  and  $3.36$ ) [3] derive from binary  $\text{Ir}_3\text{Mg}_{13}$  [4]. The peculiar crystal chemical feature for all these phases is In/Mg mixing, and thus, magnesium does not behave like a typical alkaline earth element.

In the magnesium-rich part of the Mg–Ir–In system we have now discovered a ternary phase that does not derive from a binary. The two intermetallics,  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$  and  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$ , belong to a homogeneity range  $\text{Ir}_{3+y}\text{Mg}_{18-x}\text{In}_{1+x-y}$  of a probable compound with ideal composition  $\text{Ir}_3\text{Mg}_{18}\text{In}$ . The synthesis, structure determination and crystal chemistry of these phases are reported herein.

## 2. Experimental

### 2.1. Synthesis

Starting materials for the preparation of the  $\text{Ir}_{3+y}\text{Mg}_{18-x}\text{In}_{1+x-y}$  compounds were iridium powder (ca. 200 mesh, Degussa–Hüls, >99.9%), a magnesium

\*Corresponding author. Fax: +49-251-83-36002

E-mail address: [pottgen@uni-muenster.de](mailto:pottgen@uni-muenster.de) (R. Pöttgen).

rod ( $\varnothing$  16 mm, Johnson–Matthey, >99.5%), and indium tear drops (Johnson–Matthey, >99.9%). Pieces of the magnesium rod (the surface was first cut on a turning lathe in order to remove surface impurities), iridium powder, and pieces of the indium tear drops were weighed in the 10Ir:80Mg:10In and 13.6Ir:81.8Mg:4.6In atomic ratios and put in glassy carbon crucibles (SIGRADUR<sup>®</sup>GAZ006). The crucible was placed in a water-cooled sample chamber of an induction furnace [5] and first heated at 1300 K for 15 min under flowing argon. The argon was purified before over titanium sponge (900 K), silica gel, and molecular sieves. After the melting procedure, the samples were cooled within 15 min to ca. 1200 K and held at that temperature for 30 min. Then the samples were cooled within 1 h to ca. 700 K and finally quenched by switching off the furnace. The weight losses after the melting and annealing procedures were always smaller than 0.1 wt.% of the sample and were most likely due to a minor evaporation of magnesium.

The samples could easily be separated from the crucibles after the annealing procedures. No obvious reactions with the crucible material were observed. The samples are stable in air over months. Powders are dark gray and single crystals show metallic luster.

## 2.2. X-ray powder diffraction

The samples were characterized through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) with  $\text{CuK}\alpha_1$  radiation and  $\alpha$ -quartz ( $a = 491.30$ ,  $c = 540.46$  pm) as an internal standard. The monoclinic lattice parameters (Table 1) were obtained from least-squares fits of the Guinier data. The correct indexing was ensured through intensity calculations [6] using the positional parameters of the structure refinements. For both samples, the lattice parameters of the powders ( $a = 979.1(2)$ ,  $b = 2197.2(4)$ ,  $c = 848.1(1)$  pm,  $\beta = 105.76(1)^\circ$  for  $\text{Ir}_{3.30}\text{Mg}_{17.96}\text{In}_{0.74}$  and  $a = 983.8(3)$ ,  $b = 2210.9(7)$ ,  $c = 849.0(2)$  pm,  $\beta = 105.72(2)^\circ$  for  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$ ) and the single crystals agreed well. As expected, the cell volume of the crystal with the larger indium content is also larger.

## 2.3. Scanning electron microscopy

The crystals investigated on the diffractometer and the bulk samples have been analyzed in a scanning electron microscope (LEICA 420i) through energy-dispersive analyses of X rays. MgO, iridium metal, and InAs were used as standards. No impurity elements heavier than sodium have been observed. The experi-

Table 1

Crystal data and structure refinements for  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$  and  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$  (space group  $C2/c$ ,  $Z=4$ )

Empirical formula	$\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$	$\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$
Molar mass (g/mol)	1155.77	1210.91
Unit cell dimensions (diffractometer data)	$a = 979.1(1)$ pm $b = 2197.4(2)$ pm $c = 848.2(1)$ pm $\beta = 105.79(1)^\circ$ $V = 1.7560$ nm <sup>3</sup>	$a = 983.39(8)$ pm $b = 2211.4(2)$ pm $c = 849.55(7)$ pm $\beta = 105.757(6)^\circ$ $V = 1.7781$ nm <sup>3</sup>
Calculated density (g/cm <sup>3</sup> )	4.37	4.52
Crystal size ( $\mu\text{m}^3$ )	$40 \times 60 \times 90$	$35 \times 70 \times 75$
Detector distance (mm)	80 mm	60 mm
Exposure time (min)	11 min	11 min
$\omega$ range; increment	$0-180^\circ$ ; $1.0^\circ$	$0-180^\circ$ ; $1.0^\circ$
Integr. param. $A$ , $B$ , EMS	13.5; 3.0; 0.010	13.5; 2.5; 0.014
Transm. ratio (max/min)	1.50	1.80
Abs. coefficient (mm <sup>-1</sup> )	26.5	25.4
$F(000)$	2023	2118
$\theta$ range for data collection	$2^\circ-32^\circ$	$2^\circ-35^\circ$
Range in $hkl$	$\pm 14$ , $-27 \leq h \leq 32$ , $\pm 12$	$\pm 15$ , $\pm 35$ , $\pm 13$
Total no. of reflections	10 742	13 383
Independent reflections	3076 ( $R_{\text{int}} = 0.0420$ )	3893 ( $R_{\text{int}} = 0.0375$ )
Reflections with $I > 2\sigma(I)$	2509 ( $R_{\text{sigma}} = 0.0358$ )	3304 ( $R_{\text{sigma}} = 0.0293$ )
Data/parameters	3076/108	3893/115
Goodness-of-fit on $F^2$	1.008	0.993
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0243$ $wR_2 = 0.0412$	$R_1 = 0.0232$ $wR_2 = 0.0465$
$R$ indices (all data)	$R_1 = 0.0368$ $wR_2 = 0.0434$	$R_1 = 0.0316$ $wR_2 = 0.0487$
Extinction coefficient	0.00024(1)	0.00062(3)
Largest diff. peak and hole	1.19 and $-1.30$ e/Å <sup>3</sup>	1.24 and $-1.79$ e/Å <sup>3</sup>

mentally determined compositions of  $15 \pm 2$  at.% Ir:  $76 \pm 2$  at.% Mg:  $9 \pm 2$  at.% In for  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$  and  $17 \pm 2$  at.% Ir:  $79 \pm 2$  at.% Mg:  $4 \pm 2$  at.% In for  $\text{Ir}_{3.30}\text{Mg}_{17.96}\text{In}_{0.74}$  were close to the compositions calculated from the structure refinements. The compositions obtained for the crystals and the bulk samples were identical within the listed error limits. No additional phases have been observed.

#### 2.4. Structure refinements

Irregularly shaped single crystals were selected from the crushed samples of the starting compositions 10Ir:80Mg:10In and 13.6Ir:81.8Mg:4.6In and first examined on Buerger precession cameras (white Mo radiation, Fujifilm BAS-1800 imaging plate system) in order to check the quality for intensity data collection. The data sets for both crystals (one from each sample) were collected at room temperature on a Stoe IPDS-II diffractometer with monochromatized  $\text{MoK}\alpha$  radiation in oscillation mode. Numerical absorption corrections were applied to the data sets. All relevant crystallographic data and details for the data collections are summarized in Table 1.

The  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$  crystal was investigated first. Careful analyses of the diffractometer data set revealed the systematic extinctions for a  $C$ -centered lattice and additionally the extinction condition  $h0l$  only observed for  $h, l = 2n$ . This leads to the space groups  $Cc$  and  $C2/c$  of which the centrosymmetric group was found to be correct during the structure refinements. The starting atomic parameters were deduced from an automatic interpretation of direct methods with SHELXS-97 [7] and the structure was refined with SHELXL-97 (full-matrix least-squares on  $F^2$ ) [8] with anisotropic displacement parameters for all atoms. The equivalent isotropic displacement parameters for some of the magnesium sites were too small, indicating a slightly higher scattering power on these positions. We have then refined the occupancy parameters in order to check for possible defects or mixing on the different Wyckoff positions. The refinements revealed full occupancy for the iridium sites for both crystals and Mg/In mixing for nine positions with between 1.2 and 14.8 at.% indium on the magnesium positions. In principle, also Ir/Mg mixing is possible, but based on all previous crystal chemical results [1–4] and the EDX data, In/Mg mixing is most probable. Two sites show full occupancy with

Table 2

Atomic coordinates and equivalent isotropic displacement parameters ( $\text{pm}^2$ ) for  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$  and  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$  (space group  $C2/c$ )

Atom	Wyckoff position	Occup./%	x	y	z	$U_{\text{eq}}$
$\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$						
Ir1	8f	100	0.23444(2)	0.05940(1)	0.15232(2)	90(1)
Ir2	4e	100	0	0.75078(1)	1/4	94(1)
Mg1	4c	100	1/4	1/4	0	122(4)
Mg2	8f	100	0.4272(2)	0.13304(8)	0.0685(2)	172(3)
Mg3	8f	100	0.2940(2)	0.06109(9)	0.4936(2)	194(3)
Mg4	8f	100	0.2597(2)	0.45308(9)	0.1774(2)	209(4)
Mg5	4a	100	0	0	0	203(5)
M6	8f	97.9(3)Mg/2.1(3) In	0.0313(2)	0.25530(8)	0.4292(2)	167(6)
Mg7	4e	100	0	0.5149(1)	1/4	153(5)
Mg8	8f	100	0.2701(2)	0.31528(8)	0.3142(2)	151(3)
Mg9	4e	100	0	0.0973(1)	1/4	165(5)
Mg10	8f	100	0.2653(2)	0.17498(7)	0.2948(2)	130(3)
Mg11	8f	100	0.4322(2)	0.36139(8)	0.0626(2)	110(3)
In	4e	69.9(4)In/30.1(4)Ir	0	0.37487(2)	1/4	113(1)
$\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$						
Ir1	8f	100	0.23423(1)	0.05903(1)	0.15181(2)	84(1)
Ir2	4e	100	0	0.74934(1)	1/4	89(1)
Mg1	4c	100	1/4	1/4	0	111(3)
Mg2	8f	100	0.4249(1)	0.13397(6)	0.0714(2)	149(2)
M1	8f	98.8(3)Mg/1.2(3)In	0.2901(2)	0.05923(6)	0.4903(2)	178(5)
M2	8f	95.5(3)Mg/4.5(3)In	0.2667(2)	0.45234(5)	0.1812(2)	186(5)
M3	4a	97.3(3)Mg/2.7(3)In	0	0	0	178(6)
M4	8f	85.2(3)Mg/14.8(3)In	0.0298(1)	0.25247(4)	0.4267(1)	155(3)
M5	4e	97.0(3)Mg/3.0(3)In	0	0.51714(7)	1/4	161(6)
M6	8f	97.5(3)Mg/2.5(3)In	0.2742(1)	0.31441(6)	0.3158(2)	156(5)
M7	4e	95.5(3)Mg/4.5(3)In	0	0.09743(8)	1/4	168(6)
M8	8f	96.4(2)Mg/3.6(2)In	0.2641(1)	0.17483(5)	0.2969(2)	134(4)
M9	8f	86.3(2)Mg/13.7(2)In	0.43465(9)	0.36199(4)	0.0648(1)	136(3)
In	4e	100	0	0.37540(1)	1/4	108(1)

$U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

magnesium and one site is exclusively filled with indium. Since the degree of Mg/In mixing was small, we suggested, that a ternary compound with the ideal composition  $\text{Ir}_3\text{Mg}_{18}\text{In}$  might exist. Such a sample was subsequently synthesized and a single crystal was investigated. These data revealed magnesium/indium mixing only for one site and minor In/Ir mixing, leading to the refined composition  $\text{Ir}_{3.30(1)}\text{Mg}_{17.96(4)}\text{In}_{0.74(4)}$ . The

Table 3

Interatomic distances (pm), calculated with the single crystal lattice parameters of  $\text{Ir}_3\text{Mg}_{17.1(1)}\text{In}_{1.9(1)}$

Ir1:	1	M3	265.7	Mg1:	2	Ir2	277.8	M6:	1	Ir2	282.7
	1	M5	268.3		2	M4	298.2		1	M4	289.8
Ir2:	1	Mg2	272.5	M3:	2	M6	298.9	M7:	2	Ir1	272.5
	1	M9	274.5		2	M8	299.2		1	Mg2	295.8
In:	1	M2	275.4	M4:	1	Ir1	272.5	M8:	1	Ir1	282.2
	1	M1	277.8		1	M8	293.8		1	Mg2	293.8
M1:	1	M7	278.7	M5:	2	M7	302.6	M9:	1	Ir1	274.5
	1	M8	282.2		2	M1	316.1		1	Ir2	292.3
M2:	1	M2	283.8	M6:	1	Ir2	295.8	M7:	2	M3	302.6
	1	M1	307.1		2	M2	321.5		2	M8	304.5
M3:	2	Mg1	277.8	M7:	2	M9	319.7	M8:	2	M9	305.0
	2	M6	282.7		2	M2	326.6		2	M1	314.0
M4:	2	M4	284.1	M8:	1	Mg1	305.7	M9:	2	M4	372.2
	2	M9	292.3		1	M4	309.3		2	M2	389.5
M5:	2	Mg2	295.8	M9:	1	M8	309.4	M7:	1	Ir1	282.2
	2	M8	295.9		1	M2	309.8		1	Mg2	293.8
M6:	2	M6	293.0	M7:	1	M9	340.9	M8:	1	Ir2	295.9
	2	M1	295.7		1	M1	341.5		1	Mg1	299.2
M7:	2	Mg2	302.3	M8:	1	M6	352.9	M9:	1	M1	301.2
	2	M4	308.1		1	Ir1	390.3		1	M7	304.5
M8:	1	M5	313.5	M9:	1	Ir2	284.1	M7:	1	M6	309.1
	2	M2	330.8		1	M4	289.8		1	M6	309.1
M9:	1	M2	275.4	M8:	1	M6	289.8	M9:	1	M4	310.2
	1	Ir1	277.8		1	Mg1	298.2		1	M9	326.5
M10:	1	In	295.7	M9:	1	M9	304.2	M8:	1	M4	329.4
	1	M2	300.1		1	In	308.1		1	M6	342.0
M11:	1	M8	301.2	M7:	1	Mg2	309.4	M9:	1	M4	345.3
	1	Ir1	307.1		1	M8	310.2		1	M4	345.3
M12:	1	M5	308.3	M8:	1	M6	312.5	M9:	1	Mg1	303.2
	1	M7	314.0		1	M7	372.2		1	M4	304.2
M13:	1	M3	316.1	M9:	2	Ir1	268.3	M8:	1	M7	305.0
	1	M6	338.9		2	Mg2	298.6		1	M9	305.9
M14:	1	M5	340.3	M7:	2	M1	308.3	M9:	1	M6	315.8
	1	Mg2	341.5		1	In	313.5		1	M3	319.7
M15:	1	Ir1	275.4	M8:	2	M2	317.9	M9:	1	M8	326.5
	1	Ir1	283.8		2	M1	340.4		1	Mg2	340.9
M16:	1	M9	293.0	M9:	2	M2	394.2	M8:	1	M2	371.9
	1	M1	300.1		1	M7	372.2		1	M4	304.2
M17:	1	Mg2	309.8	M7:	2	Ir1	268.3	M9:	1	M7	305.0
	1	M5	317.9		2	Mg2	298.6		1	M9	305.9
M18:	1	M3	321.5	M8:	2	M1	308.3	M9:	1	M6	315.8
	1	M6	325.1		1	In	313.5		1	M3	319.7
M19:	1	M3	326.6	M9:	2	M2	317.9	M8:	1	M8	326.5
	1	In	330.8		2	M1	340.4		1	Mg2	340.9
M20:	1	M9	371.9	M7:	2	M2	394.2	M8:	1	M2	371.9
	1	M7	389.5		1	M7	372.2		1	M4	304.2
M21:	1	M5	394.2	M8:	1	M6	352.9	M9:	1	M1	301.2
	1	M5	394.2		1	Ir1	390.3		1	M7	304.5

The *M* sites show mixed magnesium/indium occupancy (see Table 2). All distances within the first coordination spheres are listed. Standard deviations are all  $\leq 0.2$  pm.

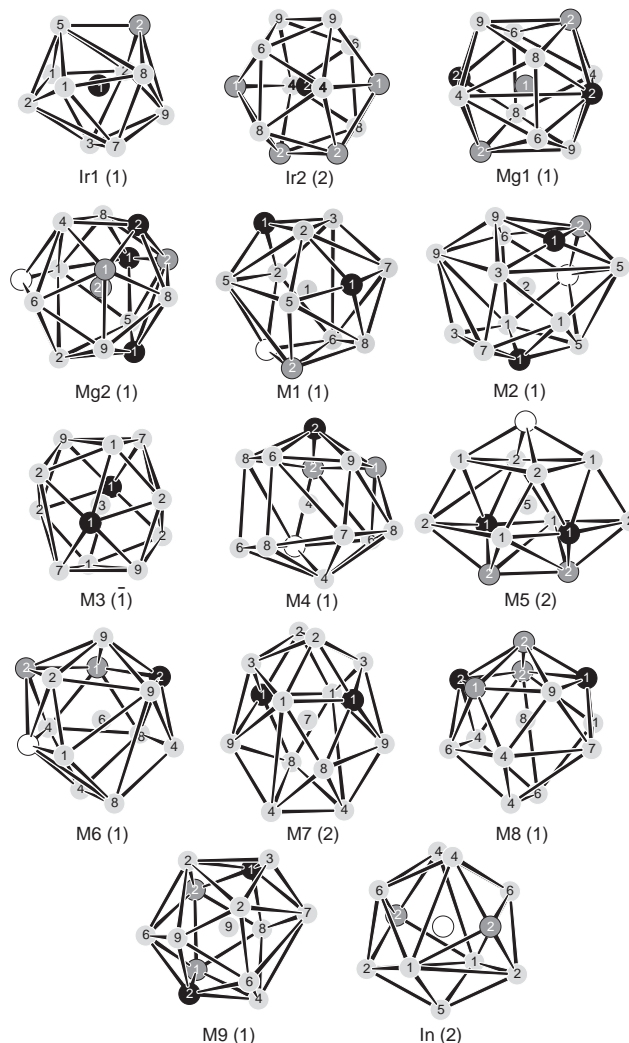


Fig. 1. Coordination polyhedra of the atoms in  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$ . The iridium, magnesium, magnesium/indium, and indium atoms are drawn as black, medium gray, light gray, and open circles, respectively. The site symmetries are indicated.

final difference Fourier syntheses were flat (Table 1). The positional parameters and interatomic distances of the refinements are listed in Tables 2 and 3. Further data on the structure refinements are available.<sup>1</sup>

### 3. Discussion

The rather complex structures of  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$  and  $\text{Ir}_{3.30}\text{Mg}_{17.96}\text{In}_{0.74}$  have 14 crystallographically independent atomic sites. The coordination polyhedra are presented in Fig. 1. The Ir1 atoms have the smallest coordination number CN10. The polyhedra of Ir2, Mg1,

<sup>1</sup>Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry Nos. CSD-414167 ( $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$ ) and CSD-414168 ( $\text{Ir}_{3.30}\text{Mg}_{17.96}\text{In}_{0.74}$ ).

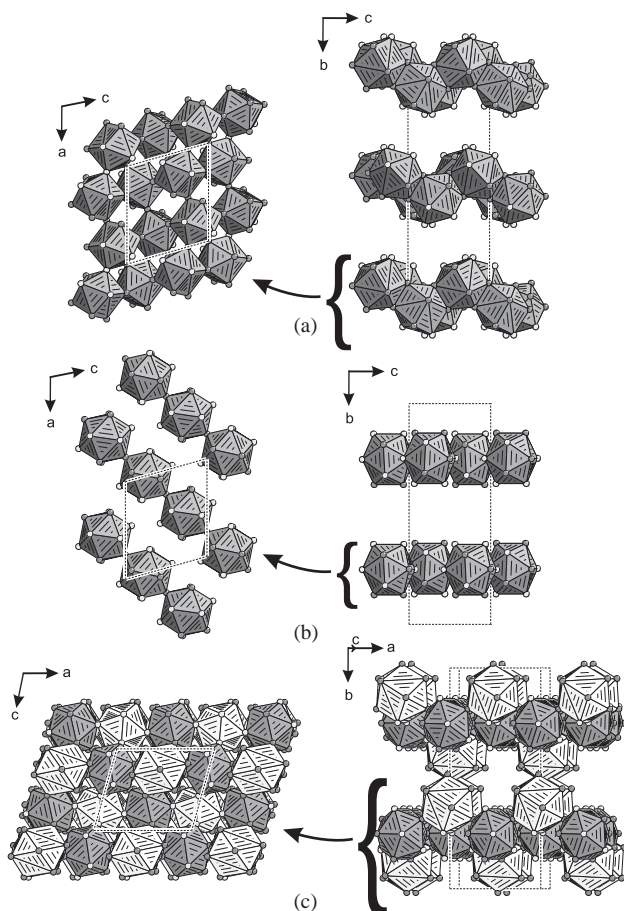


Fig. 2. The crystal structure of  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$ : (a) cutout of the structure emphasizing the condensation of the CN10 polyhedra around the Ir1 atoms at  $y$  around 0 and  $1/2$ ; (b) substructure of condensed distorted icosahedra around the Ir2 atoms at  $y \sim 1/4$  and  $y \sim 3/4$ ; (c) condensation of the CN11 polyhedra of the indium atoms and the layers of the Ir2 icosahedra.

$\text{Mg}_2$ ,  $M_1$ ,  $M_2$ , and  $M_3$  have CN12 or CN14 and they can be considered as distorted Frank–Kasper polyhedra [9,10]. The remaining sites have CN11 up to CN14 and only smaller fragments of these polyhedra derive from the Frank–Kasper polyhedra. All magnesium and  $M$  sites have at least one iridium neighbor in their coordination shell. This is different for the  $4e$  indium site. Indium has only magnesium or magnesium/indium atoms as nearest neighbors.

One way to illustrate the relatively complex crystal structure is the description via condensed polyhedra. If we consider only the polyhedra of the two crystallographically independent iridium sites and the indium atoms, we can describe the whole structure, since these three polyhedra include all other atoms. In the upper and middle part of Fig. 2 we present the connection of the Ir1 and Ir2 polyhedra. The CN10 polyhedra of Ir1 are condensed via common edges and corners forming slightly puckered layers around  $y \sim 0$  and  $y \sim 1/2$ . The icosahedra of the Ir2 atoms are condensed via two

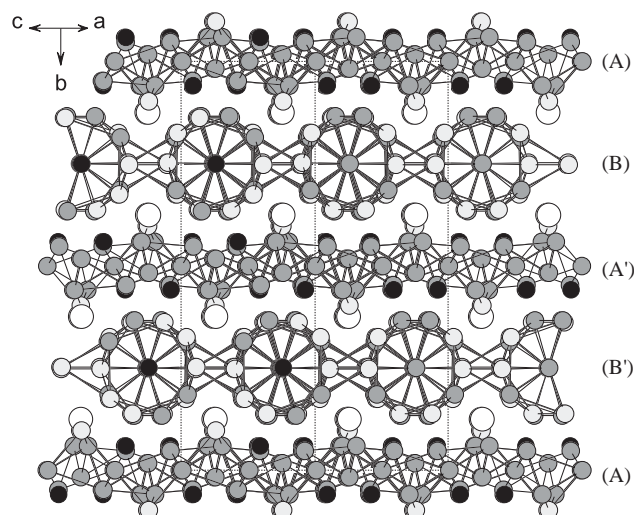


Fig. 3. View of the  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$  structure approximately along the [101] direction. The iridium, magnesium, magnesium/indium, and indium atoms are drawn as black, medium gray, light gray, and open circles, respectively. The structure is composed of the layers  $A$ ,  $B$ ,  $A'$ , and  $B'$ . The layers  $A$  and  $A'$  as well as  $B$  and  $B'$  have the same composition; however, they are shifted due to the  $C$ -centered lattice. For details see text.

common corners leading to one-dimensional strands approximately in the [101] direction (Fig. 2, middle). The centers of these polyhedra are around  $y \sim 1/4$  and  $y \sim 3/4$ . These polyhedra are condensed with the CN11 polyhedra of the indium atoms as emphasized in the lower part of Fig. 2. The remaining space between this complex arrangement is filled by the Ir1 polyhedra shown in the upper part.

In Fig. 3, we present a view of the  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$  structure approximately along the [101] direction. Considering the shorter Ir–Mg, Ir–In, and Mg–Mg interactions, it is evident that the structure is composed of the layers  $A$ ,  $B$ ,  $A'$ , and  $B'$  with different motifs. The layers  $A$  and  $A'$  as well as  $B$  and  $B'$  have the same composition; however, they are shifted due to the  $C$ -centered lattice. An interesting feature of this drawing is the position of the  $4e$  indium site. These indium atoms are located approximately between the two different kinds of layers. Both types of layers are connected via further Mg/Mg and Ir/Mg contacts.

The Ir–Mg(In) distances cover the range from 266 to 307 pm. The smaller of these distances compare well with the sum of the covalent radii of 262 pm [11], while the longer ones compare well with the Ir–Mg distances in the hexagonal Laves phase  $\text{MgIr}_2$  (300–304 pm) [12]. A very large range (275–394 pm) is observed for the Mg–Mg(In) distances. Some of these distances are significantly shorter than the average Mg–Mg distance of 320 pm in hcp magnesium [13]. This is similar to the structures of  $\text{Mg}_{2.30(1)}\text{Ir}_{2.70(1)}$  [14],  $\text{MgIr}_2$  [12], and  $\text{Ir}_3\text{Mg}_{13}$  [4].

Finally, we need to discuss the homogeneity range. The first crystal of this structure type showed mixed Mg/In occupancies for nine sites with between 1.2% and 14.8% indium on the magnesium positions. Such mixed Mg/In occupancies have been observed in various other  $\text{Ir}_x(\text{Mg}_{1-y}\text{In}_y)_z$  intermetallics [1–3,14]. The refinement of the second crystal showed, that these sites can also exclusively be occupied by magnesium atoms. The indium site is somewhat peculiar. In  $\text{Ir}_3\text{Mg}_{17.1}\text{In}_{1.9}$  this site is fully occupied, while a mixed In/Ir occupancy is observed in  $\text{Ir}_{3.30}\text{Mg}_{17.96}\text{In}_{0.74}$ . Both, the Mg/In and the Ir/In mixing lead to the homogeneity range  $\text{Ir}_{3+y}\text{Mg}_{18-x}\text{In}_{1+x-y}$ . Thus, it should be possible to synthesize also a compound with the ideal composition  $\text{Ir}_3\text{Mg}_{18}\text{In}$ ; however, all crystals we selected from samples with the ideal starting composition showed a small degree of Ir/In mixing on the 4e site.

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