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# Complex intermetallic compounds in the Mg–Ir system solved by powder diffraction

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**Abstract.** The crystal structures of two new topologically close-packed intermetallic compounds, MgIr (*Cmca*, 25 atoms) and  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  ( $x=0.067$ , *C2/m*, 11 atoms) were fully characterized by high resolution synchrotron powder diffraction and global optimization of a structural model in direct space. The simulated annealing algorithm (in parallel tempering mode) and computer program *Fox* were used.

## Introduction

In the Mg–Ir phase diagram [1] only the composition interval of 0–25 at.-% Ir is reported. Recently, two groups [2] independently discovered new phase  $\text{Mg}_{1+x}\text{Ir}_{1-x}$  ( $x = 0-0.054$ ) and could characterize the crystal structure of this compound on the basis of powder and single crystal X-ray diffraction. The iridium-rich part of the binary magnesium-iridium system was later reinvestigated, and a new binary compound with the refined composition of  $\text{Mg}_{2+x}\text{Ir}_{3-x}$  ( $x = 0.3$ ) with monoclinic  $\text{V}_2(\text{Co}_{0.57}\text{Si}_{0.43})_3$  structure type was reported [3] from single crystal X-ray diffraction. Here we report on an independent structural characterization of these two compounds, MgIr and  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ , as observed by X-ray powder diffraction.

## Experiment and Results

### Synthesis

Details of MgIr synthesis are given in [2].  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  was first observed as a by-product during the synthesis of MgIr. The final sample was prepared by sintering from element powders, with the nominal composition of  $\text{Mg}_2\text{Ir}_3$ . Compressed pellet was sealed in a steel

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ampoule with 1 bar of Ar and heated in a furnace at 1070 K for 2 h, then annealed at 870 K during 1 week and quenched in a cold water. No single crystals were obtained. Electron Probe MicroAnalysis (EPMA) has shown the composition of  $\text{Mg}_{42(6)}\text{Ir}_{58(6)}$  and Ir metal as impurity.

### Powder diffraction

Synchrotron powder diffraction data of both compounds were obtained at the Swiss-Norwegian Beam Line (SNBL) at the ESRF Grenoble (sample in a 0.2 mm glass capillary, six analyser crystals detector). Details of the data collection are given in table 1.

### Structure solution and refinement

The crystal structures of both compounds were solved and refined using the synchrotron powder diffraction data. First 26 (MgIr) and 25 ( $\text{Mg}_{2-x}\text{Ir}_{3+x}$ ) observed reflections were used for indexing by using the program DICVOL91 [4]. An orthorhombic cell with Figures-of-Merit  $M = 13.2$  and  $F = 108.0(0.0024, 101)$  was found for MgIr and monoclinic with Figures-of-Merit  $M = 14.6$  and  $F = 18.3(0.0091, 150)$  for  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ . The refined values of lattice parameters from a final Rietveld refinement are given in table 1. From the analysis of MgIr powder pattern the extinction symbol  $C\text{-}c(ab)$  was concluded corresponding to the space groups  $C2cb(41)$  and  $Cmca(64)$ . The centrosymmetric group  $Cmca$  was used for the structure solution of MgIr. From the analysis of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  powder pattern the extinction symbol  $C1\text{-}1$  was concluded corresponding to the space groups  $C2(5)$ ,  $Cm(8)$  and  $C2/m(12)$ . The centrosymmetric group  $C2/m$  was used for the structure solution of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ .

Table 1. Data collection parameters and crystal data of MgIr and  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ .

| Formula                              | MgIr           | $\text{Mg}_{2-x}\text{Ir}_{3+x}$ , $x=0.067(2)$ |
|--------------------------------------|----------------|-------------------------------------------------|
| space group                          | $Cmca$         | $C2/m$                                          |
| $a$ [Å]                              | 18.46948(6)    | 18.5699(2)                                      |
| $b$ [Å]                              | 16.17450(5)    | 5.18715(4)                                      |
| $c$ [Å]                              | 16.82131(5)    | 8.49233(6)                                      |
| $\beta$ [°]                          |                | 97.2209(5)                                      |
| $V$ [Å <sup>3</sup> ]                | 5025.11(3)     | 811.54(1)                                       |
| Wavelength [Å]                       | 0.50012        | 0.49969                                         |
| $\mu$ [mm <sup>-1</sup> ]            | 38.8           | 47.9                                            |
| Density(calc.) [g cm <sup>-3</sup> ] | 10.95          | 13.02                                           |
| $2\theta$ interval [°]               | 2.215 - 41.890 | 1.024 - 36.580                                  |
| $\chi^2$                             | 3.02           | 1.50                                            |
| $R_{wp}$ (bgr. corrected)            | 0.094          | 0.144                                           |
| $R_B$ (all reflections)              | 0.056          | 0.056                                           |

The structures of both compounds were solved by the global optimization of structural models in direct space using the simulated annealing (in parallel tempering mode) and the program *Fox* [5]. As a cost function, the integrated  $R_w$  factor [5] and anti-bump function (based on minimal distances  $\text{Mg-Ir} = 2.7$  and  $\text{Mg-Mg} = 2.8$  Å) weighted 0.55/0.45 were used. As both crystal structures were expected to be closely packed, the expected volume per atom was estimated as 15–20 Å<sup>3</sup>. No density measurements were available, and no indication of structural relations with a known structure types were found from the analysis of the cell parameters. First, we have localized iridium atoms using the advantage of *Dynamical Occupancy Correction* [5] in automatic identification of the special crystallographic positions and of merging excess atoms. In next runs localized iridium atoms were kept fixed, and free magnesium atoms were introduced subsequently till all magnesium atoms were localized. For the correct solution the integrated  $R_w$  was 0.09 and 0.15 for  $\text{MgIr}$  and  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ , resp.

The crystal structures of both compounds were refined by the Rietveld method using the synchrotron data and the program *FullProf.2k* [6]. Iridium metal was identified as an impurity in both samples. The background was interpolated between fixed points in both refinements. The runs were performed where the occupancies of individual atomic sites were refined. In  $\text{MgIr}$  all sites refined to a full occupancy and no mixed sites were observed. In  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  one magnesium site (see the discussion) has shown a mixed occupancy with iridium. The refined composition is  $\text{Mg}_{1.933(2)}\text{Ir}_{3.067(2)}$ .

In the final run of  $\text{MgIr}$  structure refinement 76 parameters were refined (main phase: 57 positional and 2 isotropic displacement, 3 cell, 7 pseudo-Voigt profile function and 1 scale parameter; impurity: 1 displacement, 1 cell, 3 pseudo-Voigt profile function and 1 scale parameter). For refined structural parameters see [2], the Rietveld plot is shown in figure 1.

When refining the structure of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  an anisotropic line broadening was observed with a clear tendency for  $0k0$  reflections being less broadened than the others. The line broadening was modeled with the pseudo-Voigt function available in the *FullProf.2k* program (profile no. 7) describing the broadening of Lorentzian part of the diffraction profile as due to the size effect and that of Gaussian part as due to the strain effect. Gaussian size and Lorentzian strain broadenings were found to be negligible. The anisotropy of size broadening was modeled by a spherical harmonics model according to the formula

$$\beta_{\mathbf{h}} = \frac{\lambda}{\cos \theta} \sum_{\text{imp}} a_{\text{imp}} y_{\text{imp}}(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}}) \quad (1)$$

where  $\beta_{\mathbf{h}}$  is the size contribution to the integral breadth of reflection  $\mathbf{h}$ , and  $y_{\text{imp}}(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}})$  are the normalized real spherical harmonics. Modeling up to the fourth order of spherical harmonics (nine coefficients  $a_{\text{imp}}$ ) appeared to be enough. Apparent crystallite size was maximal in the  $\mathbf{b}$ -axis direction (4250 Å) and much lower in directions perpendicular to the  $\mathbf{b}$ -axis (between 670 and 2000 Å). The anisotropy of strain broadening was modeled by the variance of a quartic form  $M_{hkl}$  in reciprocal space according to [7]

$$\sigma^2(M_{hkl}) = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L \quad (2)$$

Nine coefficients  $S_{HKL}$  were refined due to the monoclinic symmetry. The maximum strain was lower in the  $b$ -axis direction (0.00046) and higher in the directions perpendicular to the  $b$ -axis (between 0.0007 and 0.00117). For more details on the size-strain analysis used with the *FullProf.2k* program see the program's manual. In the final run of  $Mg_{2-x}Ir_{3+x}$  structure refinement 54 parameters were varied (main phase: 26 positional and 2 isotropic displacement, 4 cell, 20 pseudo-Voigt profile function and 1 scale parameter; impurity: 1 scale parameter). For refined structural parameters see table 2, the Rietveld plot is shown in figure 1.

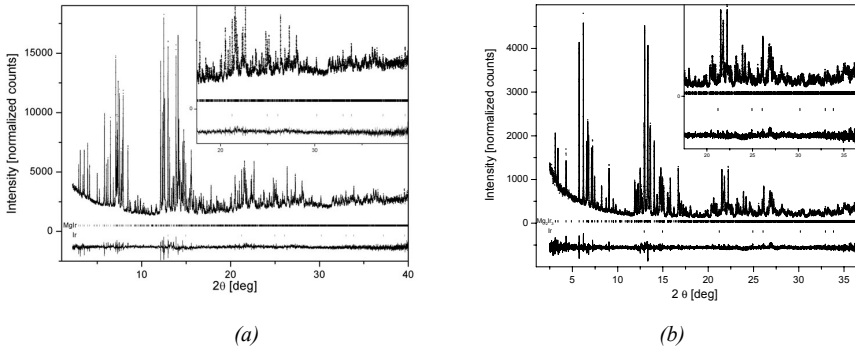


Figure 1. Rietveld plots of  $MgIr$  (a) and  $Mg_{2-x}Ir_{3+x}$  (b).

Table 2. Atom positional and displacement parameters for  $Mg_{2-x}Ir_{3+x}$ .

| atom | site | $x$        | $y$       | $z$       | $B[\text{\AA}^2]$ |
|------|------|------------|-----------|-----------|-------------------|
| Ir1  | 8j   | 0.40951(9) | 0.2357(3) | 0.2957(2) | 0.51(1)           |
| Ir2  | 8j   | 0.16756(9) | 0.2496(4) | 0.2271(2) | $=B_{Ir1}$        |
| Ir3  | 4i   | 0.8702(2)  | 0         | 0.0294(3) | $=B_{Ir1}$        |
| Ir4  | 4i   | 0.1351(2)  | 0         | 0.4655(3) | $=B_{Ir1}$        |
| Ir5  | 4i   | 0.2144(2)  | 0         | 0.7408(3) | $=B_{Ir1}$        |
| Ir6  | 2c   | 0          | 0         | 1/2       | $=B_{Ir1}$        |
| Mg7  | 4i   | 0.025(1)   | 0         | 0.174(2)  | 0.6(1)            |
| M8   | 4i   | 0.4228(5)  | 0         | 0.007(1)  | $=B_{Mg7}$        |
| Mg9  | 4i   | 0.286(1)   | 0         | 0.435(2)  | $=B_{Mg7}$        |
| Mg10 | 4i   | 0.281(1)   | 0         | 0.067(2)  | $=B_{Mg7}$        |
| Mg11 | 4i   | 0.562(1)   | 0         | 0.382(2)  | $=B_{Mg7}$        |

$$M = Mg_{0.833(5)}Ir_{0.167(5)}$$

## Discussion and Conclusions

### Crystal chemistry

Both compounds can be classified as topologically close-packed phases as the coordination of nearly all atoms has a form of Frank-Kasper polyhedra. It is quite difficult to relate the MgIr crystal structure with structures of other known intermetallic compounds. For more discussion see [2].

The structure of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  is a binary variant of the type  $\text{V}_2(\text{Co}_{0.57}\text{Si}_{0.43})_3$ . It is the second representative of this type. Interestingly the mixed Co/Si sites in the silicide corresponds to the iridium sites in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ , and vanadium sites to the magnesium sites and mixed site *M8*. All iridium sites in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  have slightly distorted icosahedral coordination, the magnesium sites and the mixed site *M8* have slightly distorted coordination by Frank-Kasper polyhedra with CN 14-16. From six magnesium sites in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  four were observed as mixed between magnesium and iridium in the single crystal study in [3], and the site *M8* was observed as fully occupied by magnesium. The refined composition is then  $\text{Mg}_{2.30}\text{Ir}_{2.70}$ , richer in magnesium than in our study where it is  $\text{Mg}_{1.933}\text{Ir}_{3.067}$ , to which corresponds the cell volume larger by 1.5% than the cell volume observed in this work. The homogeneity range of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  is probably quite large, however, it necessary to notice that the samples from [3] corresponds to 1270 K, and that from this work to 870 K, due to different annealing procedures.

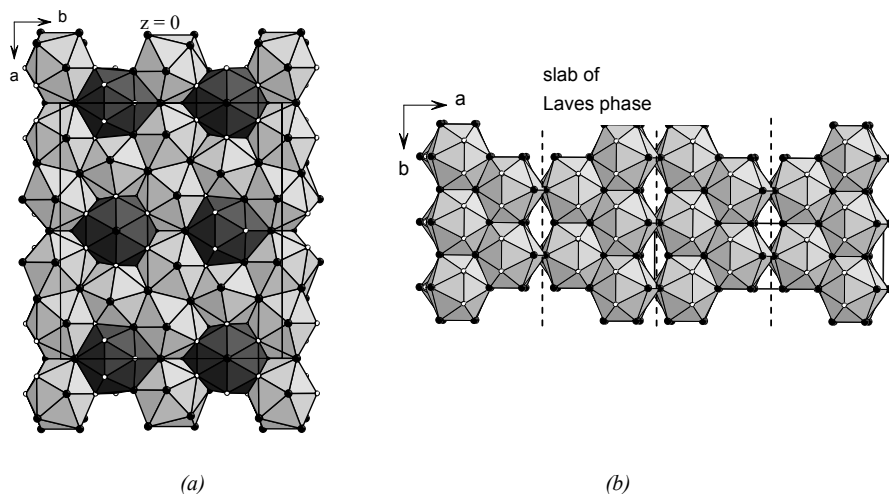


Figure 2. (a) Structural slab of MgIr. (b) Projection of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  structure along the c-axis showing (100) slabs derived from  $\text{MgIr}_2$  Laves phase. Polyhedra: Ir-centered icosahedra in light grey, Mg-centered Frank-Kasper polyhedron with CN=16 in dark grey. Ligand atoms: Ir as small white and Mg as larger black spheres.

The structure of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  can be also viewed (see figure 2) as build from (100) slabs derived from hexagonal Laves phase  $\text{MgIr}_2$  [8] ( $\text{MgZn}_2$  type, observed also by us). The slabs are derived by a distortion of iridium-centered  $\text{Mg}_6\text{Ir}_6$  icosahedra and by interchanging one magnesium and iridium site compared to the Laves phase. The lattice parameters  $b$  and  $c$  of  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  that correspond to lattice parameters  $a$  and  $c$  of the Laves phase  $\text{MgIr}_2$ , resp., are slightly larger in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  due to the structural distortion.

Anisotropic line broadening observed in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$  and explained mainly as due to anisotropic size effect can be now understood from stacking of Laves phase-like slabs: In  $a$ -axis direction the slabs are interrupted by planar faults (see figure 2),  $b$ -axis direction is without faults, and with shortest periodicity. Consequently the apparent crystallite size is largest in  $b$ -axis direction and smallest in  $a$ -axis direction.

The interatomic distances Ir–Ir cover the range of 2.45–2.66 Å in  $\text{MgIr}$  and of 2.53–2.74 Å in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ , and, to the best of our knowledge, are the shortest ones ever observed. These Ir–Ir contacts are significantly shorter than the sum of the covalent radii for two iridium atoms (2.54 Å), and than the distances in *fcc* iridium (2.72 Å). We can assume significant Ir–Ir bonding in both compounds. These short Ir–Ir distances are also shorter than those usually observed in iridium cluster compounds (2.63–2.73 Å). The Mg–Mg distances are in the range of 2.85–3.73 Å in  $\text{MgIr}$  and of 2.75–3.42 Å in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ . Most of the Mg–Mg distances are shorter than the average Mg–Mg distance of 3.20 Å in *hcp* magnesium. The shortest distance of 2.75 Å is that between the mixed occupied site *M8* and *Mg10*. The Mg–Ir distances are in the range of 2.57–3.51 Å in  $\text{MgIr}$  and of 2.76–3.17 Å in  $\text{Mg}_{2-x}\text{Ir}_{3+x}$ . Considering the course of the interatomic distances, we can assume more or less isotropic and strong bonding within both compounds.

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