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Letter

Structure refinement of $AuMg_3$, $IrMg_3$ and $IrMg_{2.8}$

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1. Introduction

We have recently redetermined the crystal structure of Mg_3Pt [1]. It has been shown that Mg_3Pt, crystallizing in the acentric space group $P6_3cm$, is isotypic with Cu_3P [2] and that the structure models proposed by Ferro and Rambaldi (Na_3As type, space group $P6_3/mmc$ [3]) and Mansmann (anti-LaF_3 type, space group $P\bar{3}c1$ [4]) are wrong.

A literature search shows that the same problems as for Mg_3Pt are obviously met for the analogous compounds $AuMg_3$ and $IrMg_3$. Schubert and Anderko [5] originally described $AuMg_3$ as isotypic with Na_3As ($a = 4.63$ Å, $c = 8.44$ Å, $Z = 2$, space group $P6_3/mmc$). In a later publication, van Look and Schubert [6] corrected this structure type assignment and proposed an anti-LaF_3 type structure for $AuMg_3$ ($a = 8.04$ Å, $c = 8.46$ Å, $Z = 6$, space group $P\bar{3}c1$). This was confirmed by Daams and van Vucht [7]. It should be noted that these researchers have also considered the possibility of a Cu_3P-type structure for $AuMg_3$. They rejected it, however, because the R value, resulting from a comparison of observed and calculated X-ray powder intensities, was slightly lower for the $P\bar{3}c1$ model (0.188) than for the $P6_3cm$ model (0.20).

Much less is known for $IrMg_3$. Ferro *et al.* [8], who obviously synthesized this compound for the first time, proposed from X-ray powder patterns an Na_3As-type structure for $IrMg_3$ ($a = 4.549$ Å, $c = 8.229$ Å, $Z = 2$, space group $P6_3/mmc$).

All previous investigations suffer from the lack of single-crystal data. We have succeeded now in the preparation of single crystals of $AuMg_3$ and $IrMg_3$ by high pressure high temperature synthesis. In this connection we found another phase with an approximate 1:3 composition in the Ir–Mg system, namely $IrMg_{2.8}$. In the present paper we describe the results of a structure refinement for these three compounds, using single-crystal X-ray data.

2. Experimental details

High pressure experiments were carried out in a modified Belt-type apparatus [9], using capsules made from tantalum and starting with stoichiometric mixtures of the elements. A homogeneous, but microcrystalline, sample of $AuMg_3$ was obtained after reaction at 12 kbar, 1400 °C (30 min) and subsequent quenching to ambient conditions. Small single crystals had been formed after the following treatment: at 12 kbar heating to 1400 °C within 10 min, cooling to 1000 °C within 30 min, to 750 °C within 70 min, subsequent quenching to ambient conditions.

In the Ir–Mg system (typical reaction conditions: 12 kbar, heating to 1400 °C within 10 min, cooling to 800 °C within 100 min, quenching) two hexagonal phases have been found around the 1:3 compositional range which were almost invariably intergrown. They exhibit the same length of the a axis (7.927(1) Å), but differ in the length of their c axes (8.190(5) and 8.560(4) Å). A variation of the reaction conditions did not result in any detectable change in the unit cell parameters. It must therefore be concluded that both phases are separate entities with a definite composition and that no solid solution range exists between them.

3. Structure analysis

After inspection of a number of crystals by Weissenberg and oscillation photographs individuals could be selected which proved to be suitable for a structure determination and were used for data collection on an Enraf-Nonius CAD-4 diffractometer. For the "$IrMg_3$" it has been found that for the two intergrown components all reflections with $l \geq 3$ were sufficiently distant to be measured separately. Consequently, reflections with $l = 0, 1, 2$ have been excluded from the final refinement. Details of the structure analysis can be taken from Table 1.

The only condition limiting possible reflections found was $l = 2n$ for $h\bar{h}0l$, pointing to a glide plane with

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TABLE 1. Crystallographic data and details of the crystal structure analysis for $AuMg_3$, $IrMg_3$ and $IrMg_{2.8}$

	$AuMg_3$	"$IrMg_3$"	
		Phase A ($IrMg_3$)	Phase B ($IrMg_{2.8}$)
Structure type	Mg_3Pt (Cu_3P)		
Space group	$P6_3cm$		
a (Å)	8.0594(3)	7.927(1)	7.927(1)
c (Å)	8.4801(5)	8.190(5)	8.560(4)
c/a	1.0522	1.0332	1.0799
V (Å^3)	477.02(7)	445.5(4)	465.9(3)
Z	6	6	6
D_x (g cm^{-3})	5.64	5.93	5.67
Crystal size (mm^3)	0.07×0.04×0.04	0.04×0.04×0.04	
Diffractometer	Enraf-Nonius CAD-4		
Scan mode	ω–2θ		
Monochromator	Graphite		
Radiation	Cu Kα	Mo Kα	
Range of intensity measurement	$2° \leq \theta \leq 70°$	$2° \leq \theta \leq 30°$	
Intensities measured	1945	2411	2340
Absorption correction	DIFABS [10]		
Correction factors (maximum, minimum)	1.552, 0.665	1.122, 0.861	1.140, 0.826
Unique reflections	193	140	116
R_{int}	0.054	0.057	0.058
Refined parameters	16	16	16
$(\Delta/\sigma)_{max}$	0.002	0.001	0.001
R, R_w	0.041, 0.039	0.064, 0.031	0.058, 0.031
$(\Delta\rho)_{max, min}$(e Å^{-3})	+2.4, −2.2	+4.2, −4.4	+6.1, −6.5

component $c/2$ in the $(11\bar{2}0)$ orientation. Together with the observed Laue class $6/mmm$ this result suggested the possible space groups $P6_3/mcm$ or $P6_3cm$. By analogy with Mg_3Pt [1], refinement in the acentric space group $P6_3cm$ gave immediately very satisfactory results.

After the isotropic refinement a numerical correction for absorption was applied to the original data sets (program DIFABS [10]) before the final refinement was performed (anisotropic for the heavy atoms, isotropic for magnesium; program system SHELX-76 [11]).

In order to obtain some information about the composition of the two components of the "$IrMg_3$" crystal investigated, we refined the site occupancy factors (SOFs) as well. The SOF for the iridium position was kept constant at 0.500 while all others were allowed to vary. Whereas for component A (with $c = 8.190$ Å) all SOFs refined to their theoretical values for a composition $IrMg_3$ within one standard deviation, the SOF of Mg(3) for component B ($c = 8.560$ Å) refined to 0.198(41), as compared with the theoretical value of 0.333. All other SOFs for component B are at their theoretical values. Therefore, a composition $IrMg_{2.8(3)}$ can be calculated for component B.

Final residuals were $R = 0.041$, $R_w = 0.039$ for $AuMg_3$, $R = 0.064$, $R_w = 0.031$ for $IrMg_3$, and $R = 0.058$, $R_w = 0.031$ for $IrMg_{2.8}$.

Atomic coordinates and displacement factors for $AuMg_3$, $IrMg_3$ and $IrMg_{2.8}$ are given in Table 2 and derived bond distances in Table 3. (Lists of observed and calculated structure factors have been prepared and may be obtained from the authors (K.-J.R.).

TABLE 2. Positional parameters and isotropic displacement factors (angstroms squared) for $AuMg_3$, $IrMg_3$ and $IrMg_{2.8}$

Atom	Site	x/a	y/b	z/c	U_{eq}/U_{iso}[a]
$AuMg_3$					
Mg(1)	6c	0.2752(18)	0.2752(18)	0.0821(39)	0.003(4)
Mg(2)	6c	0.3754(17)	0.3754(17)	0.4275(36)	0.010(4)
Mg(3)	4b	1/3	2/3	0.2101(31)	0.019(5)
Mg(4)	2a	0	0	0.3248(48)	0.012(7)
Au	6c	0.3288(3)	0.3288(3)	0.75(fixed)	0.004(1)
$IrMg_3$					
Mg(1)	6c	0.2820(37)	0.2820(37)	0.0695(37)	0.013(5)
Mg(2)	6c	0.3663(28)	0.3663(28)	0.4131(26)	0.006(4)
Mg(3)	4b	1/3	2/3	0.1918(53)	0.043(16)
Mg(4)	2a	0	0	0.2915(54)	−0.003(10)
Ir	6c	0.3274(4)	0.3274(4)	0.75 (fixed)	0.006(1)
$IrMg_{2.8}$					
Mg(1)	6c	0.2758(37)	0.2758(37)	0.0890(32)	0.016(5)
Mg(2)	6c	0.3605(31)	0.3605(31)	0.4227(19)	0.007(5)
Mg(3)[b]	4b	1/3	2/3	0.2103(65)	0.064(29)
Mg(4)	2a	0	0	0.3069(58)	−0.018(11)
Ir	6c	0.3295(6)	0.3295(6)	0.75 (fixed)	0.007(2)

[a] U_{eq} for gold and iridium is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[b] The SOF for Mg(3) refined from the theoretical value of 0.333 to 0.20(4), resulting in a composition $IrMg_{2.8}$.

TABLE 3. Selected interatomic distances (angstroms) for $AuMg_3$, $IrMg_3$ and $IrMg_{2.8}$

	$AuMg_3$	$IrMg_3$	$IrMg_{2.8}$
Au/Ir–Mg(4)	2.725(10)	2.617(5)	2.657(10)
–Mg(3)	2.726(4) (2×)	2.708(9) (2×)	2.680(9) (2×)
–Mg(2)	2.760(31)	2.771(19)	2.813(17)
–Mg(2)	2.819(19)	2.777(22)	2.868(20)
–Mg(1)	2.845(20) (2×)	2.848(26) (2×)	2.791(26) (2×)
–Mg(1)	2.849(34)	2.641(31)	2.933(28)
–Mg(2)	3.229(18) (2×)	3.068(19) (2×)	3.116(19) (2×)
–Mg(1)	3.494(18)	3.431(25)	3.419(25)
Mg(1)–Au/Ir	2.845(20) (2×)	2.848(25) (2×)	2.791(24) (2×)
–Au/Ir	2.849(34)	2.641(31)	2.933(28)
–Mg(2)	3.014(24) (2×)	2.928(29) (2×)	2.954(29) (2×)
–Mg(4)	3.026(37)	2.881(39)	2.874(41)
–Mg(2)	3.039(45)	2.892(37)	2.934(33)
–Mg(4)	3.111(38)	3.190(42)	3.258(45)
–Mg(3)	3.142(19) (2×)	3.037(29) (2×)	3.078(31) (2×)
–Au/Ir	3.494(18)	3.431(25)	3.419(25)
Mg(2)–Au/Ir	2.760(31)	2.771(19)	2.813(17)
–Au/Ir	2.819(19)	2.777(22)	2.868(20)
–Mg(1)	3.014(25) (2×)	2.928(32) (2×)	2.954(33) (2×)
–Mg(1)	3.039(45)	2.892(37)	2.934(33)
–Mg(1)	3.106(24)	3.068(31)	3.215(31)
–Mg(3)	3.134(26) (2×)	3.105(32) (2×)	3.125(38) (2×)
–Mg(4)	3.149(18)	3.069(24)	3.025(26)
–Au/Ir	3.229(18) (2×)	3.068(19) (2×)	3.116(20) (2×)
–Mg(3)	3.487(29) (2×)	3.402(35) (2×)	3.539(43) (2×)
Mg(3)–Au/Ir	2.726(4) (3×)	2.708(9) (3×)	2.680(9) (3×)
–Mg(2)	3.134(26) (3×)	3.105(32) (3×)	3.125(38) (3×)
–Mg(1)	3.142(19) (3×)	3.037(29) (3×)	3.078(31) (3×)
–Mg(2)	3.487(30) (3×)	3.402(36) (3×)	3.539(42) (3×)
Mg(4)–Au/Ir	2.725(10) (3×)	2.617(7) (3×)	2.657(10) (3×)
–Mg(1)	3.026(37) (3×)	2.881(39) (3×)	2.874(41) (3×)
–Mg(1)	3.111(38) (3×)	3.190(42) (3×)	3.258(45) (3×)
–Mg(2)	3.149(18) (3×)	3.069(24) (3×)	3.025(26) (3×)

4. Discussion

The results of the structure refinement show that $AuMg_3$, $IrMg_3$ and $IrMg_{2.8}$ are isostructural with Mg_3Pt and hence with Cu_3P as well. The structure models previously proposed for these compounds are wrong. For a complete discussion of the structure the reader is referred to refs. 1 and 2.

The slightly negative values of the isotropic displacement factors for Mg(4) in $IrMg_3$ and $IrMg_{2.8}$ could be explained by a partial replacement of magnesium by iridium in the 2a position. From a refinement of the SOFs a composition $Mg_{1.9(2)}Ir_{0.1(2)}$ instead of $Mg_{2.0}$ could indeed be calculated. This deviation from the ideal stoichiometry, however, is less than one standard deviation. We believe, therefore, that the negative displacement factors are due to an insufficient correction for absorption rather than to a replacement of magnesium by iridium in the 2a position.

At present there is no convincing explanation for the surprising finding that two basically isostructural phases exist in the Ir–Mg system near the 1:3 composition, with no solid solution range between them, namely $IrMg_3$ and $IrMg_{2.8}$. Further work on intermetallic phases in the Ir-Mg system is in progress.

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