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Cubic $Mg_{29}Ir_4$ crystallizing with an ordered variant of the Mg_6Pd-type structure

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Abstract

$Mg_{29}Ir_4$ was synthesised by solid state reaction at 500°C and characterised by X-ray powder diffraction. Its structure (space group $F\bar{4}3m$, $a = 20.1148(3)$ Å, $Z = 12$) corresponds to a fully ordered variant of the Mg_6Pd type.

Keywords: Intermetallic compounds; Crystal structure; Powder diffraction

1. Introduction

Magnesium-rich transition metal (T) compounds having the approximate composition Mg_6T are known to form with T = Ru, Rh, Pd, Ir and Pt [1]. They crystallize with two types of cubic face-centred structures which have the same space group ($F\,\bar{4}\,3\,m$), similar cell parameters (~20 Å), but slightly different atom arrangements. One structure is represented by Mg_6Pd [2] and contains 396 atoms per unit cell. The atoms occupy 14 independent sites of which one shows mixed occupancy by 51% Mg and 49% Pd. The other structure (called the Na_6Tl-type structure [3]) is represented by $Mg_{44}Rh_7$ [4], $Mg_{44}Ir_7$ [5] and $Mg_{6.2\text{-}6.6}Ru$ [6] and contains 408 atoms per unit cell. The atoms also occupy 14 independent sites but only 12 of them correspond to sites occupied in the Mg_6Pd-type structure. The structure refinements for the Rh and Ir phases suggest fully ordered structures whereas the Ru phase reveals two sites having mixed occupancy. The major difference between the two structure types is that in $Mg_{44}Rh_7$ all T sites are surrounded by magnesium in icosahedral configuration, whereas in Mg_6Pd about one third of the T sites are surrounded by magnesium in tricapped trigonal prismatic configuration. Stereo views illustrating these differences can be consulted in Ref. [2].

The compounds were originally synthesised from the elements by melting at high temperature and subsequent annealing [1]. During our work on ternary metal hydrides based on magnesium and transition elements [7] we obtained some of these phases by a solid state reaction (sintering). For the Ir sample the observed X-ray powder diffraction pattern was not in agreement with the structure data published for $Mg_{44}Ir_7$ [5]. We therefore investigated that sample in more detail. As will be shown below, it was found to contain a more magnesium-rich phase of composition $Mg_{29}Ir_4$. Its structure is ordered and differs significantly from $Mg_{44}Ir_7$.

2. Experimental

A sample of nominal composition Mg/Ir = 12 was prepared by sintering a mixture of element powders (Ir, Johnson-Matthey 99.9% purity; Mg, CERAC 99.6% purity) pressed into a pellet. The pellet was wrapped in a tantalum foil and placed in a quartz tube which was sealed with an internal pressure of Argon of 40 kPa. The tube was heated at 500°C for two weeks in a resistive furnace and then quenched in water. The reaction product consisted of a fragile dark grey pellet with a metallic appearance. It was ground in an agate mortar, passed through a 50 μm mesh and studied by X-ray diffraction on a Guinier diffractometer. About 10 mg of the powder was mixed with a tiny drop of "3

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Table 1
Data collection parameters

Radiation type, source, power	X-rays, Cu, 35 kV 40 mA
Wavelength	Cu $K_{\alpha 1}$, $\lambda = 1.5405981$ Å
Diffractometer	Huber G645
Geometry	Guinier, asymmetric transmission
Monochromator	Johansson-Guinier, Ge(111)
Receiving-slit width	0.1 mm
Temperature of measurement	25°C
Angular range (2θ)	7° to 100°
Step (2θ)	0.02°
Counting time	20 s/step
Specimen motion	translation, 1 Hz
Resolution	$FWHM_{min}$ $Mg_{29}Ir_4$ = 0.09° 2θ
Resolution of a standard	$FWHM_{min}$ SiO_2 = 0.065° 2θ

in 1®" oil and uniformly spread on a thin polyethylene film which was covered with a second foil and secured on the specimen carrier with a circular clamp. The information relative to the data collection are summarised in Table 1.

A second data set with silicon (SRM640a [8], $a = 5.430825(36)$ Å) as internal standard was measured for the determination of the cell parameter. The positions of the peaks were refined with the program SHADOW [9] by using a Voigt profile, and corrected with a second order polynomial. The cell parameter was refined to $a = 20.1148(3)$ Å (average $|\Delta 2\theta| = 0.0038$Å) with the program LATCON of the XTAL3.2 system [10] from 35 peaks with $28° < 2\theta < 80°$

Table 2
Refined structural parameters for $Mg_{29}Ir_4$

Atom	Site	x	y	z	U_{iso} (10^{-2} Å^2)
Ir1	16*e*	0.1510(1)	x	x	086(5)
Ir2	16*e*	0.4172(1)	x	x	U Ir1
Ir3	16*e*	0.6584(1)	x	x	U Ir1
Mg1	48*h*	0.0516(4)	x	0.1600(6)	1.9(1)
Mg2	48*h*	0.0989(5)	x	0.7725(6)	U Mg1
Mg3	48*h*	0.1084(5)	x	0.2812(6)	U Mg1
Mg4	48*h*	0.1548(4)	x	0.5209(6)	U Mg1
Mg5	48*h*	0.1917(4)	x	0.0187(6)	U Mg1
Mg6	24*g*	0.1422(8)	1/4	1/4	U Mg1
Mg7	24*g*	0.6171(7)	1/4	1/4	U Mg1
Mg8	24*f*	0.3211(9)	0	0	U Mg1
Mg9	16*e*	0.5524(6)	x	x	U Mg1
Mg10	16*e*	0.9196(7)	x	x	U Mg1
Mg11	4*a*	0	0	0	U Mg1

Space group: $F\bar{4}3m$ (N° 216); Pearson code: cF396. All sites have full occupancy.
$a = 20.1148(3)$ Å, $V = 8138.6(3)$ Å^3, $Z = 12$, $D_x = 3.60$ g/cm^3 Pseudo-Voigt η parameter: 0.33(5).
Final agreement indices: $R_{wp} = 11.1\%$, $S = 2.1$, $R_{Bragg} = 4.35\%$ for 260 reflections.

Table 3
Ir-Mg interatomic distances and shortest Mg-Mg contacts (Å)

Ir1	−3 Mg6 2.822(3)	Ir3	−3 Mg7 2.735(5)
	−3 Mg1 2.83(1)		−3 Mg4 2.78(1)
	−3 Mg3 2.89(1)		−3 Mg2 2.85(1)
	−3 Mg5 2.90(1)		
Ir2	−3 Mg3 2.83(1)	Mg11	−4 Mg10 2.80(1)
	−3 Mg9 2.85(1)		
	−3 Mg4 2.92(1)		
	−3 Mg8 3.05(1)		

3. Structure refinement

The structure was refined by the Rietveld method, using the program DBWS-9006PC [11] which was locally adapted to deal with the Guinier geometry. The atomic form factors and anomalous dispersion correction terms were those included in the program. No absorption correction was done. The background was evaluated by linear interpolation between 24 points and held fixed during the refinement process. The individual profiles were calculated up to 10 FWHM on each side of the peaks. The starting values for the positional parameters of $Mg_{29}Ir_4$ were those of Mg_6Pd [2]. Elementary magnesium was the only impurity detected and was included in the two-phase refinement. In the final stages of the refinement 35 parameters were allowed to vary simultaneously: 27 for $Mg_{29}Ir_4$ (one scale factor, one cell parameter, U, V and W for the usual Caglioti function, one asymmetry factor for the peaks below 25° (2θ), one pseudo-Voigt mixing parameter η, 18 atomic coordinates and two isotropic temperature factors), five for the magnesium impurity phase (one scale factor, two cell parameters, V and W) and three coefficients for a parabolic correction of the 2θ scale. Since no significant substitution or partial occupancy was found to occur on any site (error limit: ~4%) all population parameters were fixed at 100%. Standardised [12] structure parameters and agreement indices are given in Table 2, and selected interatomic distances in Table 3. The observed, calculated and difference Rietveld plots are presented in Fig. 1.

4. Discussion

The $Mg_{29}Ir_4$ phase (87.9 at.% Mg) is richer in magnesium than the previously reported $Mg_{44}Ir_7$ phase [4] (83.6 at.% Mg). Its structure has many common features with, but also differs significantly from that of $Mg_{44}Ir_7$. Both structures are fully ordered and have 12 (out of 14) atom sites in common. Among the common sites two are occupied by different atom sorts: the Ir3 and Mg7 sites in $Mg_{29}Ir_4$ correspond to magnesium and iridium sites, respectively, in $Mg_{44}Ir_7$. As to the sites which are not common between the two structures, the Mg1 site in $Mg_{29}Ir_4$ is empty in

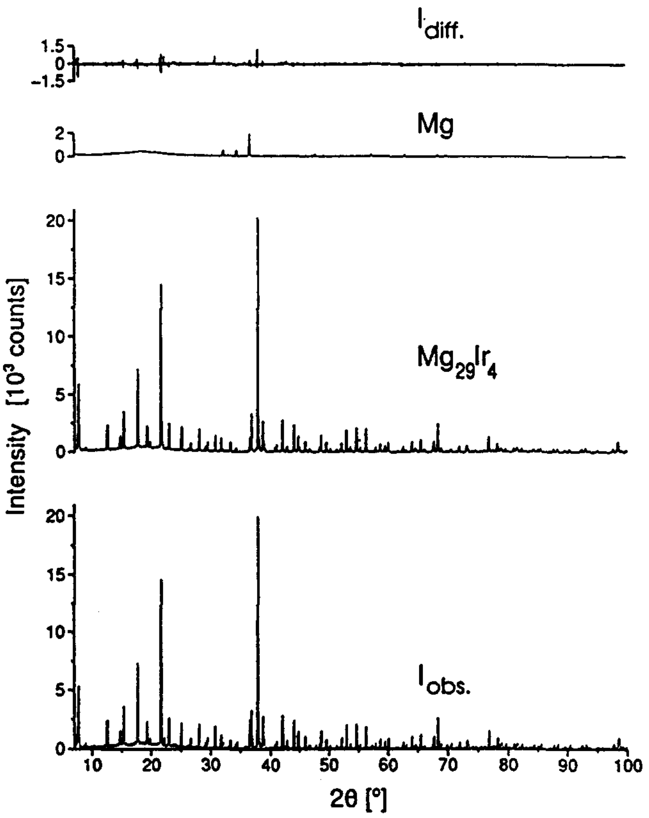

Fig. 1. Observed (bottom), calculated (middle) and difference (top) X-ray diffraction patterns for $Mg_{29}Ir_4$ and the magnesium impurity phase.

$Mg_{44}Ir_7$, and one of the magnesium sites in $Mg_{44}Ir_7$ (Mg8 in the notation of Ref. [4]) is empty in $Mg_{29}Ir_4$. Thus the atom coordinations around iridium are significantly different in the two structures. In $Mg_{44}Ir_7$ the three iridium sites have twelve-fold icosahedral coordination by magnesium with average Ir-Mg distances of 2.91, 2.90 and 2.88 Å, respectively. In $Mg_{29}Ir_4$ two iridium sites (Ir1 and Ir2) have icosahedral magnesium coordination with average Ir-Mg distances of 2.91 and 2.86 Å, respectively, whereas one (Ir3) has a nine-fold tricapped trigonal prismatic magnesium coordination with a smaller average Ir-Mg distance of 2.78 Å.

The $Mg_{29}Ir_4$ structure can be regarded as an ordered variant of the (partially disordered) Mg_6Pd type structure. The mixed site in the latter corresponds to the ordered Mg10 site in the former. That site forms four tetrahedra per unit cell which are centred by Mg11. The distances Mg11-Mg10 = 2.80 Å are the shortest Mg-Mg contacts in the structure.

$Mg_{29}Ir_4$ was synthesised at the nominal composition Mg/Ir = 12 and found to be in equilibrium at 500°C with magnesium only, which indicates that it is the most magnesium-rich compound in this system. Intermetallic phases with stoichiometries and structures intermediate to $Mg_{44}Ir_7$ and $Mg_{29}Ir_4$ have not yet been obtained and further studies are needed to clarify this part of the Mg-Ir phase diagram.

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