

A redetermination of the crystal structure of trimagnesium platinum, Mg₃Pt*

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Abstract

Single crystals of Mg₃Pt have been obtained from the elements by high pressure–high temperature reaction in a modified Belt-type apparatus. The compound crystallizes hexagonally, space group $P6_3cm$, with $a=7.9103(8)$ Å, $c=8.3223(16)$ Å, $c/a=1.0521$ and $Z=6$. The structure refinement ($R=0.027$, $R_w=0.022$ for 264 absorption-corrected reflections) shows unequivocally that Mg₃Pt is isostructural with Cu₃P and that the structure models proposed by Ferro and Rambaldi (Na₃As type, space group $P6_3/mmc$) and Mansmann (anti-LaF₃ type, space group $P\bar{3}c1$) are wrong.

1. Introduction

No phase diagram is available for the Mg–Pt system [1, 2]. Ferro and Rambaldi [3] reported two intermediate phases, namely a homogeneous solid solution around the Mg₆Pt composition and a stoichiometric compound Mg₃Pt. Two more intermediate phases have been reported by Stadelmaier and Hardy [4], namely an MgPt compound and an ordered f.c.t. phase near 75 at.% Pt. According to Bronger and Klemm [5], two cubic superlattice phases, MgPt₃ and MgPt₇, exist on the platinum-rich side of the Mg–Pt system.

The available structural information on Mg₃Pt is based on its X-ray powder pattern. Ferro and Rambaldi [3] indexed the pattern assuming a hexagonal unit cell ($a=4.577$ Å, $c=8.322$ Å, $c/a=1.818$, space group $P6_3/mmc$) and proposed a structure by analogy with Na₃As [6]. Because the Na₃As type has been described [6] as nearly anti-isomorphic with the LaF₃ (tysonite) type, discussions with respect to the true unit cell size and space group of the latter have influenced the Na₃As and therefore also the Mg₃Pt discussion.

The most important result in the present context is that a triple hexagonal cell ($a'=3^{1/2}a$, $c'=c$) seems to be accepted for LaF₃ [7–9]. In contrast to

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Oftedal [7], who postulated space group $P6_3/mcm$ for LaF_3 , however, Mansmann [8] and Zalkin *et al.* [9] found the space group $P\bar{3}c1$ to be the correct one.

Mansmann [10] applied his results for LaF_3 to Cu_3P and proposed a structure in space group $P\bar{3}c1$ for this compound. By analogy he suggested the same space group (and structure) for compounds such as Mg_3Pt as well. Olofsson [11], however, in a very careful single-crystal study, was able to show that Cu_3P crystallizes in the acentric space group $P6_3cm$ and that there is no need to lower the Laue symmetry from hexagonal to trigonal.

As far as the structural relations between Mg_3Pt and Na_3As , LaF_3 or Cu_3P , if there are indeed any, are concerned, three main questions have to be answered in the course of a structure determination.

(i) Is the correct hexagonal unit cell the small (a, c) or the triple one ($a' = 3^{1/2}a, c' = c$)?

(ii) Is the correct Laue class $6/mmm$ or $\bar{3}m1$?

(iii) Is the correct space group centric or acentric?

Evidently, single-crystal X-ray data are needed to solve the problem.

Unfortunately, during the preparation of Mg–Pt alloys difficulties arise from the relatively low boiling point of magnesium compared with the high melting temperature of platinum. As a consequence, all Mg–Pt alloys reported to date were known only in microcrystalline form. We have now succeeded in the preparation of Mg_3Pt single crystals by synthesis in a closed high pressure system. This method avoids the vaporization losses of magnesium inevitably found in normal pressure experiments and allows for a rather exact control of composition even at the very high temperatures which are needed for single-crystal growth. The method has been successfully applied before for the synthesis of intermetallic phases in other systems with highly volatile components (KAu_2 [12], NaPt_2 [13], Mg_2PtSi [14], AlMg_3Pt_2 [15], $\text{Pd}_8\text{Al}_{21}$, $\text{Pd}_8\text{Al}_{17}\text{Si}_4$ and $\text{Pt}_8\text{Al}_{21}$ [16], Al_3Au_8 [17], $\text{Al}_{11}\text{Au}_6$ and AlAu [18], AlAu_4 [19]).

2. Experimental details

Mg_3Pt was synthesized by reaction of a stoichiometric mixture of the elements in a modified Belt-type high pressure apparatus [20]. The reaction product obtained at 12.5 kbar and 1400 °C (tantalum capsule, reaction time 30 min, subsequent quenching to ambient conditions) was microcrystalline, homogeneous Mg_3Pt , as proved by microscopic investigation and X-ray powder patterns (Huber Guinier system 600; Stoe Stadi P device with position-sensitive detector).

High pressure reaction at the same p, T conditions for 10 min with subsequent slow cooling to 1000 °C (60 min) and quenching to ambient conditions resulted in an ingot containing small single crystals, which proved suitable for a crystal structure analysis.

A crystal fragment (approximate dimensions $0.06 \times 0.02 \times 0.02 \text{ mm}^3$) was used for data collection on an Enraf-Nonius CAD-4 diffractometer (Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator in incident beam). Lattice parameters were refined from 2θ values of 25 reflections in the range $8.9^\circ \leq \theta \leq 16.4^\circ$. Intensities were measured for $2 \leq \theta \leq 30^\circ$ ($\omega - 2\theta$ scan technique, scan width $(0.70 + 0.35 \tan \theta)^\circ$). Three standard reflections showed an intensity loss of 3.5% during data collection. An experimental correction for absorption was applied based on ψ scans; relative transmission factors varied between 70.2% and 99.9%. The total number of measured intensities ($(\sin \theta_{\max})/\lambda = 0.70 \text{ \AA}^{-1}$; $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $0 \leq l \leq 11$) was 2792, all of which were used for the subsequent calculations (programme system SHEL-X 76).

3. Structure analysis

From X-ray film and diffractometer data the triple hexagonal unit cell with $a = 7.9103(8) \text{ \AA}$ and $c = 8.3223(16) \text{ \AA}$ was found to be the correct one for Mg_3Pt . Therefore the smaller unit cell with space group $P6_3/mmc$ and hence the Na_3As -type structure proposed by Ferro and Rambaldi [3] can be excluded with certainty.

The only condition limiting possible reflections found was $l = 2n$ for $h\bar{h}0l$, pointing to a glide plane with component $c/2$ in $(11\bar{2}0)$ orientation. Merging of the 2792 collected intensities according to Laue classes $6/mmm$ and $\bar{3}m1$ gave 264 ($R_{\text{int}} = 0.025$) and 445 ($R_{\text{int}} = 0.024$) unique reflections respectively. The result of the data reduction strongly suggested Laue class $6/mmm$ and therefore, according to the reflection conditions, $P6_3/mcm$ or $P6_3cm$ as possible space groups. In addition, space group $P\bar{3}c1$ was also included in the calculations in order to check Mansmann's proposal [10].

Oftedal's parameters [7] for tysonite were used as starting values for the anisotropic refinement in space group $P6_3/mcm$. Convergence was reached after a few cycles at $R = 0.115$ and $R_w = 0.101$ (Table 1). The rather high values of the residuals as compared to the low value of R_{int} , the high electron densities in the final difference Fourier map and especially the very high anisotropic displacement factors for some atoms (U_{11} for $\text{Mg}(1)$, U_{33} for $\text{Mg}(2)$ and $\text{Mg}(3)$; see Table 1) make it evident that this structure solution is not more than just a first approximation of the true structure.

Refinement in space group $P\bar{3}c1$ showed the same overall picture. Here again the residuals after anisotropic refinement, the features in the final difference Fourier map and some of the anisotropic displacement factors have relatively high values (Table 1). It can therefore be concluded that both centric space groups $P6_3/mcm$ and $P\bar{3}c1$ are not appropriate for Mg_3Pt .

A change to the acentric space group $P6_3mc$, however, avoided all the difficulties described and gave immediately very satisfactory refinement results. The residuals dropped considerably and anisotropic refinement was possible without any problems.

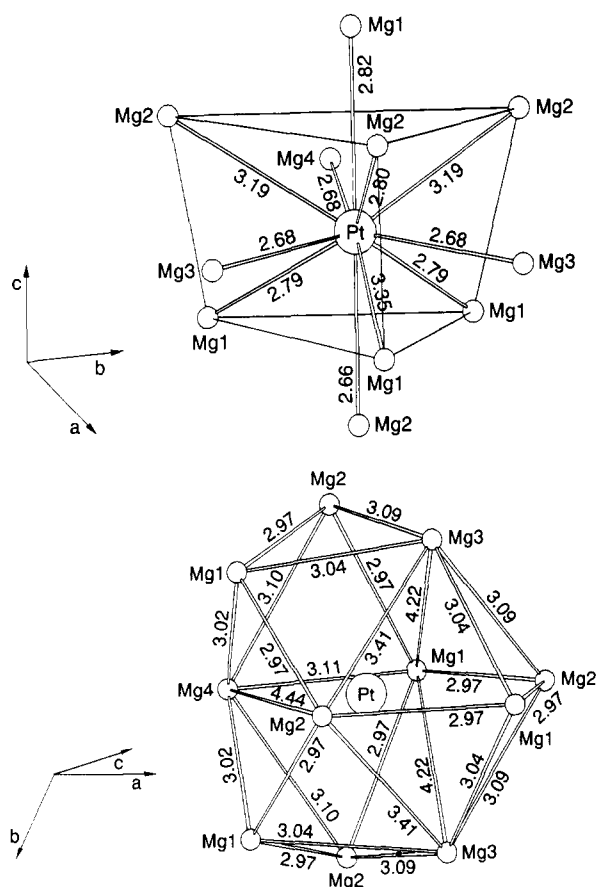


Fig. 1. Two different views on the coordination polyhedron around platinum.

At this stage a numerical correction for absorption was applied to the original 2792 data (programme DIFABS [21]; correction factors min. 0.902, max. 1.200; R_{int} after merging of the corrected data, 0.019) before performing the final anisotropic refinement. Final residuals were $R = 0.027$ and $R_w = 0.022$ ($w = 1/\sigma^2(F)$) for 24 refined parameters and 264 unique reflections (including unobserved ones). The maximum shift-error ratio in the final refinement cycle was less than 0.001; the maximum features in the final difference Fourier synthesis were 2.3 and $-3.0 \text{ e } \text{\AA}^{-3}$.

Atomic coordinates and anisotropic displacement factors for Mg_3Pt are given in Table 2 and derived bond distances in Table 3*.

*A list of observed and calculated structure factors has been prepared and may be obtained from the authors (K.-J.R.).

TABLE 1

Results of structure refinement in the wrong space groups $P6_3/mcm$ and $P\bar{3}c1$

Space group $P6_3/mcm$							
Atomic parameters and selected anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$)							
	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	
Mg(1)	12k	0.6835(37)	0.6835(37)	0.0787(40)	1634(264)	407(177)	270(121)
Mg(2)	4c	1/3	2/3	1/4	145(76)	145(76)	10315(2363)
Mg(3)	2a	0	0	1/4	-54(78)	-54(78)	3382(689)
Pt	6g	0.6587(3)	0.6587(3)	3/4	99(11)	29(16)	58(9)
$R = 0.1147, R_w = 0.1006$							
$\Delta\rho_{\max} = 13.2 \text{ e \AA}^{-3}, \Delta\rho_{\min} = -11.8 \text{ e \AA}^{-3}$							
Space group $P\bar{3}c1$							
Atomic parameters and selected anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$)							
	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	
Mg(1)	12g	0.0106(29)	0.3242(30)	0.0784(29)	1962(228)	748(112)	118(67)
Mg(2)	4d	1/3	2/3	0.2028(32)	568(87)	568(87)	297(137)
Mg(3)	2a	0	0	1/4	-115(47)	-115(47)	3057(653)
Pt	6f	0.6588(2)	0.6588(2)	1/4	88(8)	38(12)	64(7)
$R = 0.1175, R_w = 0.0960$							
$\Delta\rho_{\max} = 12.6 \text{ e \AA}^{-3}, \Delta\rho_{\min} = -12.6 \text{ e \AA}^{-3}$							

4. Discussion

The results of the present single-crystal study show unequivocally that the acentric space group $P6_3cm$ is indeed the correct one for Mg_3Pt . Therefore the structural models proposed by Ferro and Rambaldi (Na_3As type, space group $P6_3/mcm$ [3]) and Mansmann (anti- LaF_3 type, space group $P\bar{3}c1$ [10]) can be excluded with certainty.

Mg_3Pt is isostructural with Cu_3P [11]. For a complete description of the structure the reader is referred to Olofsson's detailed discussion in ref. 11.

The most important interatomic distances in Mg_3Pt can be taken from Table 3. Platinum is surrounded by 11 magnesium atoms at distances ranging from 2.663 to 3.350 \AA ($\langle\text{Pt-Mg}\rangle = 2.875 \text{ \AA}$) (Fig. 1). The coordination numbers for Mg(1) to Mg(4) are 12 (8 Mg + 4 Pt), 13 (9 Mg + 4 Pt), 12 (9 Mg + 3 Pt) respectively.

For Cu_3P a small range of homogeneity has been found [22–24]. We tried to get some information about the composition of the single crystal of Mg_3Pt used from a refinement of the site occupancy factors (SOFs). The SOF for the platinum position was kept constant while the others were allowed to vary. The results are shown in Table 4. All SOFs for the magnesium positions showed values lower than theoretical, for Mg(3) and Mg(4) with

TABLE 2
Crystallographic data for Mg₃Pt

		Atomic parameters		
		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Hexagonal, space group <i>P6₃cm</i> (no. 185)				
<i>a</i> = 7.9103(8) Å, <i>c</i> = 8.3223(16) Å, <i>c/a</i> = 1.0521				
<i>V</i> = 450.98(19) Å ³ , <i>Z</i> = 6, <i>F</i> (000) = 684				
Mg(1)	6c	0.2850(18)	0.2850(18)	0.0868(26)
Mg(2)	6c	0.3756(14)	0.3756(14)	0.4332(25)
Mg(3)	4b	1/3	2/3	0.2134(17)
Mg(4)	2a	0	0	0.3290(38)
Pt	6c	0.3278(1)	0.3278(1)	0.75(fixed)

Anisotropic displacement parameters (Å ² × 10 ⁴)					
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Mg(1)	114(35)	502(133)	53(59)	−9(62)	251(66)
Mg(2)	386(76)	33(61)	104(67)	177(112)	16(31)
Mg(3)	97(24)	97(24)	161(90)	0	49(12)
Mg(4)	153(46)	153(46)	206(114)	0	76(23)
Pt	66(4)	62(7)	66(4)	−46(14)	31(4)

TABLE 3
Mg₃Pt: selected interatomic distances (angstroms)

Pt–Mg(2)	2.663(21)		Mg(1)–Pt	2.794(14)	(2 ×)
Mg(4)	2.675(8)		Pt	2.823(21)	
Mg(3)	2.676(2)	(2 ×)	Mg(2)	2.971(29)	
Mg(1)	2.794(15)	(2 ×)	Mg(2)	2.973(18)	
Mg(2)	2.798(14)		Mg(2)	2.974(18)	(2 ×)
Mg(1)	2.823(21)		Mg(4)	3.024(27)	
Mg(2)	3.190(13)	(2 ×)	Mg(3)	3.036(14)	(2 ×)
Mg(1)	3.350(14)		Mg(4)	3.112(28)	
Mg(2)–Pt	2.663(21)		Mg(3)–Pt	2.676(2)	(3 ×)
Pt	2.798(14)		Mg(1)	3.036(14)	(3 ×)
Mg(1)	2.971(29)		Mg(2)	3.087(17)	(3 ×)
Mg(1)	2.973(18)		Mg(2)	3.409(19)	(3 ×)
Mg(1)	2.974(19)	(2 ×)			
Mg(3)	3.087(17)	(2 ×)	Mg(4)–Pt	2.675(8)	(3 ×)
Mg(4)	3.095(14)		Mg(1)	3.024(27)	(3 ×)
Pt	3.190(13)		Mg(2)	3.095(14)	(3 ×)
Mg(3)	3.409(19)		Mg(1)	3.112(28)	(3 ×)

TABLE 4

Results of refinement of the site occupancy factors for the magnesium positions in Mg₃Pt

Position	Site occupancy factor	
	Theoretical	Experimental
Mg(1)	0.500	0.491(14)
Mg(2)	0.500	0.497(12)
Mg(3)	0.333	0.294(8)
Mg(4)	0.167	0.149(7)
Pt	0.500	0.500(fixed)

5 and 2.5 standard deviations respectively. However, the positional parameters and the final R values did not change significantly. From the refined SOFs a composition Mg_{2.86(8)}Pt can be calculated for the investigated single crystal. This value is close to the ideal stoichiometry Mg_{3.00}Pt within two standard deviations. Therefore the question of a possible range of homogeneity for "Mg₃Pt" still remain open.

Finally, it should be noted that substitution of one of the three magnesium atoms in Mg₃Pt by silicon yielded the intermetallic compound Mg₂PtSi [14]. Mg₂PtSi crystallizes in an ordered ternary variant of the Na₃As structure (space group $P6_3/mmc$, $a = 4.254 \text{ \AA}$, $c = 8.542 \text{ \AA}$).

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