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A Palladium-Magnesium Alloy Phase of Co_2Al_5 Type

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The crystal structure of hexagonal $PdMg_{\sim 2.8}$ has been determined and refined by least-squares technique on the basis of three dimensional X-ray data. The structure is of the Co_2Al_5-type. The phase exhibits a range of homogeneity. The dimensions of the unit cell vary over the ranges $a = 8.646-8.660$ Å and $c = 8.175-8.169$ Å. The coordination and the interatomic distances are discussed.

The phases $PdMg_{5.6-6.8}$, $PdMg_4$, $PdMg_3$, $PdMg_{\sim 2.7}$, PdMg, and Pd_3Mg have been discussed by Ferro.[1] His results were obtained from powder and single crystal investigations. Ferro found that $PdMg_{\sim 2.7}$ is hexagonal with cell constants in the intervals $a = 8.644-8.663$ Å and $c = 8.160-8.170$ Å, increasing with the palladium content. He also found that the alloys were heterogeneous at the composition Pd_2Mg_5, but suggested that complete homogeneity was reached only after very long periods of annealing. Information about the equilibrium diagram of the magnesium-palladium system has been given by Savitskii *et al.*[2]

EXPERIMENTAL

The alloys were prepared from palladium sponge and magnesium filings, both with impurities less than 0.1 %. Mixtures were compacted under a pressure of 2000 atm into lumps, weighing 0.3–0.5 g, which were then induction-heated in a covered alumina crucible. The atmosphere in the furnace was argon at a pressure of about 400 mm Hg and the time of the melting operation was about 10 sec at 1700–1800°C. The lumps were crushed and subsequently annealed for three weeks at 400°C in small iron capsules which were enclosed in silica tubes containing an argon atmosphere. The heat-treatment was discontinued by quenching of the tubes in water.

The densities were calculated from the weight of the samples in air and in chloroform. The alloy samples were analyzed gravimetrically for palladium with dimethylglyoxime as a precipitating reagent.[3] The analysis showed that some magnesium was lost in the melting process.

X-Ray powder diffraction photographs of the alloys in the composition range $PdMg_{2.0-6.0}$ were taken with a Guinier focusing camera with monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å). KCl was added as an internal standard ($a = 6.2919$ Å at 20°C).[4] Lattice parameters were calculated by the program PIRUM.[5]

Single crystal data were registered with CuK radiation in a Weissenberg camera by rotation of the crystal around the c-axis. The intensities were not corrected for absorption because of the small size of the crystal, $0.03 \times 0.04 \times 0.04$ mm³, and the fact that the

shape was almost spheric with many small faces. Five layer lines were registered by multiple film technique. 110 independent intensities were obtained as average values from a total number of 567 visually estimated reflexions.

The computational work was mainly carried out on a CD 3600 machine. Raw data were processed by the program DRF, subroutine INCOR,[6] which calculated Lp factors. The structure was refined by the least-squares program LALS.[6] The original program, UCLALS 1, has been modified by Zalkin and in Uppsala by Lundgren, Liminga and Brändén. The calculation of interatomic distances was done by the program DISTAN.[7]

RESULTS OF POWDER WORK

Powder patterns of samples at the composition $PdMg_{2.5-3.0}$ showed the existence of a hexagonal phase, for reasons developed below designated Pd_2Mg_5, with cell constants in the intervals: $a=8.646-8.660$ Å and $c=8.175-8.169$ Å. The values thus obtained for the c-axis are in fair agreement with those reported by Ferro.[1] For the a-axis, however, the results are at variance. The present study has shown the length of this axis as well as the cell volume to increase with increasing content of magnesium in contrast to the data reported by Ferro. The single crystal was picked from a sample with the cell constants:

$$a = 8.6598 \pm 6 \text{ Å} \quad (20°C)$$
$$c = 8.1688 \pm 9 \text{ Å}$$

In some samples powder patterns of more than one phase were observed. In magnesium-rich samples $PdMg_{\sim 2.5}$ occurred together with $PdMg_3$ and in palladium-rich samples, together with PdMg. A tabulation of known phases containing palladium and magnesium is given in Table 1 and powder data of $PdMg_{\sim 2.5}$ in Table 2.

The mean atomic volume of different phases as a function of atomic percent magnesium has been calculated and is illustrated in Fig. 1. (Mean atomic volume=cell volume divided by the number of atoms in the unit cell.) The cubic phase, $PdMg_{5.6-6.8}$, shows a negative deviation from the curve including all other phases.

Table 1. Tabulation of known phases containing Pd and Mg. The structure of $Pd_{1.1}Mg_{0.9}$ has been described by Kripyakevich and Gladyshevskii [11] and the other values within parentheses are those of Ferro.

Phase	Crystal system	Structure	a (Å)	c (Å)	Z (formula units per unit-cell)
Pd_3Md	cubic	disordered	(3.907—3.920)	—	1
PdMg	cubic	CsCl-type	3.175 (3.16—3.17)	—	1
$Pd_{1.1}Mg_{0.9}$	tetr.	AuCu-type	(3.02)	(3.41)	1
Pd_2Mg_5	hex.	Co_2Al_5-type	8.646—8.660 (8.644—8.663)	8.175—8.169 (8.160—8.170)	4
$PdMg_3$	hex.	Na_3As-type	4.609 (4.613)	8.420 (8.410)	2
$PdMg_4$	no information published				
$PdMg_{5.6-6.8}$	cubic	—	20.056 (20.06)	—	(60)

Table 2. Powder data of $PdMg_{\sim 3.5}$

$\sin^2\theta = (0.010548 \pm 2)\cdot(hk+kl+lh)+(0.008891 \pm 2)\cdot(l^2)$
$a = 8.6598 \pm 6$ Å
$c = 8.1688 \pm 9$ Å

I_{obs}	$h\ k\ l$	$\sin^2\theta_{obs} \times 10^5$	$\sin^2\theta_{calc} \times 10^5$	$\Delta \sin^2\theta \times 10^5$
st	1 0 0	1053	1054	− 1
m	1 0 1	1910	1943	−33
st	0 0 2	3556	3556	0
w	2 0 0	4206	4219	−13
st	2 0 1	5116	5108	8
w	2 1 0	7386	7384	2
w	2 0 2	7773	7775	− 2
w	2 1 1	8304	8273	31
w	3 0 0	9512	9493	19
st	3 0 1	10385	10382	3
st	2 1 2	10945	10940	5
m	2 0 3	12219	12221	− 2
w	2 2 0	12653	12658	− 5
w	0 0 4	14223	14225	− 2
m	3 1 1	14601	14602	− 1
w	1 0 4	15262	15280	−18
w	2 2 2	16233	16214	19
w	3 0 3	17498	17495	3
w	2 1 4	21599	21609	−10
vw	3 1 3	21733	21715	18
w	3 2 2	23593	23598	− 5
w	2 0 5	26461	26447	14
st	2 2 4	26904	26884	20
w	3 3 0	28495	28481	14
w	3 0 5	31721	31721	0
w	3 3 2	32054	32037	17
vst	5 1 1	33582	33589	− 7
w	5 0 3	34335	34373	−38

REFINEMENT OF THE STRUCTURE

The symmetry and the systematic absences ($hh\bar{2}\bar{h}l$ with $l=2n+1$) exhibited by the single crystal X-ray data of Pd_2Mg_5 are characteristic for the space groups $P6_3/mmc$, $P\bar{6}2c$, and $P6_3mc$. These three space groups have also been

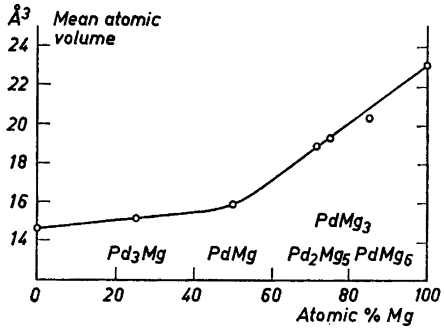

Fig. 1.

Table 3. Observed and calculated structure factors.

h	k l	F_{obs}	F_{calc}	h	k l	F_{obs}	F_{calc}
0	2 0	164.3	−214.9	1	1 2	67.7	− 84.4
0	3 0	166.3	−162.4	1	2 2	356.9	336.4
0	4 0	184.2	−184.3	1	5 2	138.0	130.0
0	5 0	81.3	− 66.1	1	6 2	85.6	75.5
0	8 0	129.4	144.0	1	7 2	134.5	−141.0
0	9 0	166.0	166.4	2	2 2	147.2	−146.2
1	1 0	67.2	68.6	2	3 2	216.6	−203.0
1	2 0	113.0	−116.2	2	6 2	155.9	165.3
1	4 0	137.9	118.3	2	7 2	101.6	109.9
1	5 0	86.0	− 77.1	3	3 2	352.8	−362.0
1	6 0	114.2	−110.5	3	4 2	119.4	104.6
1	7 0	231.4	238.4	3	5 2	89.2	95.8
1	8 0	81.2	87.9	4	−1 2	63.7	60.2
2	2 0	417.9	440.1	4	1 2	96.1	−100.4
2	3 0	171.4	148.2	4	5 2	65.5	57.2
2	6 0	95.7	− 99.1	5	5 2	162.5	−164.0
3	1 0	51.0	− 46.7	0	1 3	60.0	− 45.7
3	3 0	607.0	497.3	0	2 3	377.9	−516.4
3	4 0	79.3	65.2	0	3 3	260.3	−275.9
3	5 0	134.4	−133.5	0	4 3	192.3	171.1
3	7 0	79.5	− 91.5	0	5 3	119.9	96.9
4	5 0	92.3	− 82.9	0	6 3	195.1	194.2
5	5 0	310.8	297.6	1	3 3	197.3	−197.6
5	6 0	136.1	142.5	1	5 3	265.9	254.4
0	1 1	58.9	− 78.6	2	3 3	81.8	− 58.4
0	2 1	296.4	371.5	2	4 3	94.4	− 82.1
0	3 1	412.3	475.6	2	7 3	82.8	− 78.7
0	4 1	77.4	− 61.7	3	5 3	263.7	−288.1
0	5 1	113.2	−102.1	3	6 3	156.9	−159.5
0	6 1	270.0	−254.5	3	7 3	137.3	152.1
0	7 1	117.0	−124.6	4	5 3	69.4	− 65.1
1	3 1	260.3	250.7	8	1 3	70.7	− 67.0
1	4 1	167.8	−154.9	0	1 4	118.0	123.7
1	5 1	237.2	−221.7	0	2 4	92.3	− 83.5
1	6 1	77.8	64.0	0	3 4	86.4	− 62.5
2	3 1	91.3	− 83.8	0	4 4	133.8	−118.6
2	5 1	170.1	172.0	0	5 4	188.2	−184.0
2	6 1	82.6	77.8	0	7 4	58.5	54.0
2	7 1	94.3	85.5	0	8 4	145.0	160.1
2	8 1	147.3	−143.6	1	1 4	95.4	94.6
3	5 1	221.2	241.0	1	2 4	161.9	−175.6
3	6 1	130.5	131.7	1	4 4	134.6	113.4
3	7 1	105.5	− 96.9	1	5 4	98.1	− 79.6
4	6 1	62.8	65.4	1	6 4	78.3	− 63.7
8	1 1	60.8	51.3	1	7 4	168.9	170.9
0	1 2	75.7	− 80.0	1	8 4	78.2	77.9
0	2 2	100.3	104.1	2	2 4	206.8	236.9
0	3 2	95.4	81.5	2	3 4	183.3	182.9
0	4 2	183.2	163.2	2	4 4	90.9	71.7
0	5 2	387.8	342.0	2	6 4	105.1	−112.7
0	6 2	78.4	72.6	3	3 4	297.6	375.7
0	8 2	153.3	−171.5	3	5 4	91.3	− 88.1
0	9 2	183.1	−189.0	5	5 4	175.8	203.2

suggested by Ferro. The structure was assumed to be isomorphous with Co_2Al_5[8] and Rh_2Al_5,[9] which both have the centrosymmetric space group symmetry $P6_3/mmc$ (No. 194), and since the radius ratio $r_{Pd}/r_{Mg}=0.86$ is very nearly that of $r_{Co}/r_{Al}=0.87$, the position parameters of the Co_2Al_5 structure were adopted as a starting point for the refinement of Pd_2Mg_5. The total number of refined parameters was 14 including 5 scale factors and 5 temperature factors. Hughes' weighting scheme was used and after six cycles of least-squares refinement the R-value had converged to 0.10. When only reflexions with F_{obs}/F_{calc} greater than 0.67 and F_{obs}/F_{calc} less than 1.50 were accepted, four reflexions were excluded from the refinement and a better R-value was obtained, $R=0.094$. In the weighting scheme the weight, w, is equal to:

$$\begin{array}{lll} 1/80^2 & \text{if} & |F_o| < 80 \text{ or} \\ 1/|F_o|^2 & \text{if} & |F_o| \geq 80 \end{array}$$

A comparison of observed and calculated structure factors is given in Table 3. The final positional and thermal parameters, together with their standard deviations, are shown in Table 4. Fourier maps showed the structure to be essentially correct, and the Fourier synthesis calculated from the difference between F_{obs} and F_{calc} was small, always less than 3.5 % of the maximum electron density calculated from F_{obs}.

DISCUSSION

The thermal parameters seem to be somewhat high for Mg(1), Mg(2), and Pd(1). Attempts have been made to explain the difference between the thermal parameters of the two heavy atoms, which both have small standard deviations. A multiplier was applied to the scattering factor of the atom Pd(1). This parameter was refined and was given a starting value of 0.1. After five cycles of least-squares refinement the parameter had increased to 0.1664 which does not differ significantly from the stoichiometric value 2/12 given in Table 4, "special positions." The product of the scattering factor multiplier for atom A in one special position and the total number of symmetry codes used in the calculation equals the number of atoms A in that position in the unit-cell.

Table 4. Atomic coordinates and thermal parameters.

Space group $P6_3/mmc$ (No. 194)
Unit-cell contents: 4 Pd_2Mg_5

Atom	Special positions	x	z	B (Å^2)
Mg(1)	2 *a*	0	0	1.74±65
Mg(2)	6 *h*	0.4588±11	1/4	1.66±39
Mg(3)	12 *k*	0.1936± 8	0.9341±12	0.93±25
Pd(1)	2 *d*	1/3	3/4	1.05±13
Pd(2)	6 *h*	0.1228±2	1/4	0.71± 7

Table 5. Interatomic distances in Pd_2Mg_5 compared to distances in Co_2Al_5 and Rh_2Al_5.

Number of neighbours	Atom	Neighbour	Distances in Pd_2Mg_5	Equivalent distances in Co_2Al_5	Equivalent distances in Rh_2Al_5
6	Mg(1)	Pd(2)	2.75	2.54	2.66
6		Mg(3)	2.94	2.62	2.68
2	Mg(2)	Pd(2)	2.75	2.41	2.45
1	■	Pd(1)	3.12	2.61	2.65
4		Mg(3)	3.14	2.74	2.81
2		Mg(2)	3.25	3.14	3.31
4		Mg(3)	3.26	2.97	3.07
1	Mg(3)	Pd(1)	2.59	2.35	2.44
1		Pd(2)	2.78	2.51	2.56
1		Mg(1)	2.94	2.62	2.68
2		Pd(2)	2.95	2.70	2.78
1		Mg(3)	3.02	2.92	3.02
2		Mg(3)	3.08	2.73	2.79
2		Mg(2)	3.14	2.74	2.81
2		Mg(2)	3.26	2.97	3.07
6	Pd(1)	Mg(3)	2.59	2.35	2.45
3		Mg(2)	3.12	2.61	2.65
2	Pd(2)	Mg(1)	2.75	2.54	2.66
2		Mg(2)	2.75	2.41	2.45
2		Mg(3)	2.78	2.51	2.56
4		Mg(3)	2.95	2.70	2.78
2		Pd(2)	3.19	2.91	3.10

The structure of Co_2Al_5 was first reported by Bradley and Cheng [8] who also gave a careful description of the atomic arrangement. The structure was later refined by Newkirk, Black and Damjanovic.[10] The structure of Pd_2Mg_5 deviates very little from that of Co_2Al_5. The interatomic distances have been calculated and can be compared with the equivalent distances in Co_2Al_5 and Rh_2Al_5, Table 5. The shortest distance, 2.59 Å, is the distance Pd(1)—Mg(3), which is considerably shorter than the Pd—Pd distance, 2.75 Å, in pure palladium metal. The shortest distance between magnesium atoms is 2.94 Å, Mg(1)—Mg(3), which differs much from the distance between magnesium atoms in the element, 3.20 Å.

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