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Crystal structure of trimagnesium monopalladium, Mg_3Pd

J. P. A. Makongo, C. Kudla, Yu. Prots, R. Niewa, U. Burkhardt and G. Kreiner*

Max-Planck-Institut fur Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

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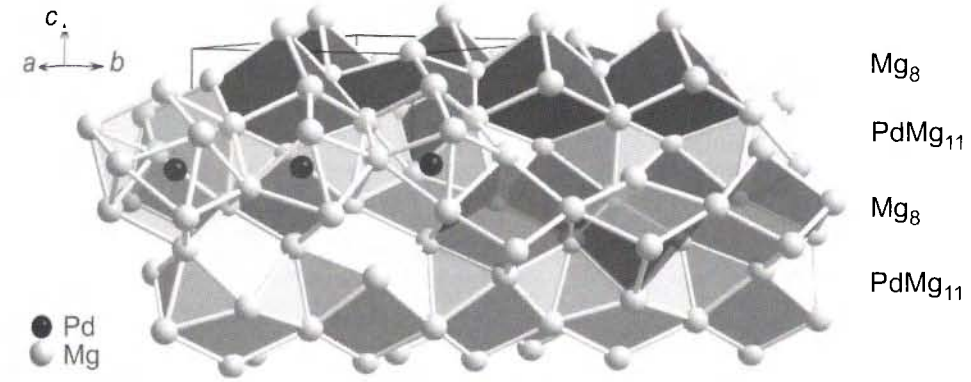

Abstract

Mg_3Pd, hexagonal, $P6_3cm$ (no. 185),
$a = 7.987(1)$ Å, $c = 8.422(1)$ Å, $V = 465.3$ Å^3, $Z = 6$,
$R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.045$, $T = 293$ K.

Source of material

Samples of the nominal composition Mg_xPd_{1-x} with $x = 0.74$, 0.75, 0.76 and 0.78 were prepared by induction melting mixtures of the elements (Pd, 99.99 %; Mg, 99.99 %) in argon filled and weld-sealed tantalum ampoules. Subsequently, the ampoules were encapsulated in fused silica tubes and annealed at 773(5) K for three weeks. Finally, the ampoules were quenched in water. A single crystal of Mg_3Pd with metallic lustre was obtained from the sample at the nominal composition $Mg_{0.78}Pd_{0.22}$.

Chemical analyses on impurities of O, N, C, H and Ta were performed using the carrier gas hot extraction, the combustion technique and ICP-MS spectroscopy, respectively. All impurities were below their respective limit of detection: O < 750 ppm, N < 150 ppm, C < 1000 ppm, H < 32 ppm, Ta < 600 ppm. The microstructures of the samples were analyzed via microscopic examination in combination with EDXS to determine the number of phases and their composition. At 78.0 at-% and 76.0 at-% Mg the samples revealed two phases, Mg_3Pd and the complex metallic alloy phase (CMA) $Mg_{78.5}Pd_{21.5}$ [1]. The sample at 75.0 at-% Mg is nearly single phase (CMA < 1%), whereas the sample at 74.0 at-% Mg consists of Mg_3Pd and Mg_5Pd_2.

Experimental details

The unit cell parameters of Mg_3Pd either in equilibrium with the CMA or the Mg_5Pd_2 phase were obtained from least-squares fittings of reflections taken from Guinier powder patterns (Huber, Ge monochromator, CuKα_1 radiation, $\lambda = 1.5405929$ Å, Si powder SRM 640c as internal standard, $a = 5.431195(9)$ Å). They are equal within the e.s.ds. The title compound exhibits no perceptible homogeneity range and undergoes a peritectic reaction at 898(3) K into Mg_5Pd_2 and the liquid phase according to DTA measurements.

* Correspondence author (e-mail: kreiner@cpfs.mpg.de)

Discussion

The intermetallic compound Mg_3Pd has been reported by Ferro [2], who assigned Na_3As as the structure type ($Z = 2$, $P6_3/mmc$). However, later investigations on MMg_3 compounds with M = Ir, Pt and Au by Range et al. [3,4] revealed that these adopt the Cu_3P structure type ($Z = 6$, $P6_3cm$). Both are space-filling arrangements of filled Edshammar polyhedra (CN 11), i.e. full-capped trigonal prisms, and empty cubes [5]. The Cu_3P structure type can be derived from the Na_3As type by a slight deformation of the CN 11 polyhedra resulting in $a' = \sqrt{3}a$ and $c' = c$.

The title compound crystallizes in the Cu_3P structure type with Pd at the centre of the Edshammar polyhedron surrounded by 11 Mg atoms at distances ranging from 2.684(1) Å to 3.431(3) Å. The Mg4 and Mg5 atoms exhibit distorted icosahedra and Mg2 (CN 13) and Mg3 (CN 12) irregularly shaped polyhedra as atomic environments. The interatomic distances d(Mg—Mg) extend from 2.993(2) Å to 3.459(2) Å. The Edshammar polyhedra $PdMg_{11}$ are arranged in layers perpendicular to their pseudo-threefold axes. By sharing common triangular faces each Edshammar polyhedron is linked to six neighboring polyhedra. These layers alternate with layers of empty, distorted Mg_8 cubes, which are bonded by the rhombic faces of the Edshammar polyhedra above and below. The distortion of the Edshammar polyhedra from ideal symmetry in the Cu_3P structure type gives rise to two crystallographic different Mg_8 cubes of nearly equal volumes (28.3 Å^3 and 28.1 Å^3).

The anisotropic displacement parameters U_{22} of Mg2 and U_{33} of Mg4 are slightly enlarged giving rise to prolate ellipsoids, which are oriented towards the respective cube centres. A refinement of a single crystal obtained from the sample at $Mg_{0.75}Pd_{0.25}$ yields for U_{22} and U_{33} the same unusual behavior. Moreover, unusual atomic displacement parameters have been reported for MMg_3 compounds with M = Ir, Pt. These findings are likely caused by intrinsic structural features, which need further detailed investigations to understand their origin. Refinements of the site occupancy factors for both single crystals yield $Mg_{2.98(1)}Pd$. In the final cycles of the refinements the composition has been fixed to ideal composition, Mg_3Pd.

Table 1. Data collection and handling.

Crystal:	silver, irregular, size 0.025 × 0.060 × 0.090 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	62.61 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	70.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6212, 715
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 707
$N(param)_{refined}$:	26
Programs:	SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	6*c*	0.32839(4)	0	0.0676(7)	0.0128(1)	0.0138(1)	0.0124(1)	$\frac{1}{2}U_{22}$	0.0013(2)	0
Mg(2)	6*c*	0.3765(2)	0	0.3954(4)	0.0214(4)	0.042(1)	0.0126(6)	$\frac{1}{2}U_{22}$	−0.0031(6)	0
Mg(3)	6*c*	0.7180(2)	0	0.2393(4)	0.0243(6)	0.0179(7)	0.0120(6)	$\frac{1}{2}U_{22}$	0.0001(5)	0
Mg(4)	4*b*	⅓	⅔	0.1126(5)	0.0130(4)	U_{11}	0.053(2)	$\frac{1}{2}U_{11}$	0	0
Mg(5)	2*a*	0	0	0	0.0131(6)	U_{11}	0.028(1)	$\frac{1}{2}U_{11}$	0	0

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